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METEORITIC, SOLAR, AND TERRESTRIAL  
RARE-EARTH DISTRIBUTIONS

by

Larry A. Haskin, Fred A. Frey, Roman A. Schmitt,  
and Richard H. Smith

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DIVISION OF  
**GENERAL DYNAMICS**

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Larry A. Haskin, \* Fred A. Frey, \* Roman A. Schmitt, †  
and Richard H. Smith†

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## INTRODUCTION

### GEOCHEMICAL PROPERTIES OF THE REE

The REE (rare earth elements) are defined for this review as the lanthanides ( $Z = 57\text{--}71$ ) and Y ( $Z = .39$ ). The lightest member of group III B of the periodic table, Sc, is excluded because its geochemical behavior is quite distinct from that of the REE (RANKAMA and SAHAMA, 1950; GOLDSCHMIDT, 1954; NORMAN, 1965). Lanthanide No. 61, Pm, has no known long-lived isotopes and is not found in nature, so its exclusion from the discussions which follow is implied.

The REE are not really rare. They are much more abundant in the lithosphere than Ag or Au, and about as plentiful as Sn, Pb, and Co. They are well dispersed, however, being components of all common rocks (EBERHARDT, 1908), and relatively few large concentrations of RE minerals are known (GOLDSCHMIDT, 1954).

AHRENS (1964a) lists a number of properties of the REE which would be expected to influence their geochemical behavior. Under normal conditions, the oxidation state for all members of the group is +3.  $\text{Ce}^{+3}$  can be oxidized to the +4 state and  $\text{Eu}^{+3}$  reduced to the +2 state under conditions which occur in nature. The ionic radii of the lanthanide series decrease regularly with increasing atomic number, a phenomenon well known as the "lanthanide contraction." The exact values of the ionic radii are close to 1 Å, and vary according to the compounds studied and their investigators. The REE are strongly electropositive and their compounds are predominantly ionic. They readily form complexes, both with organic and inorganic ligands.

Geochemically, the REE are strictly lithophile. The metals and their oxides are non-volatile, and somewhat refractory. These qualities

help to reduce the number of assumptions necessary for the interpretation of abundance data from natural materials.

The chemical properties of the various REE are so similar that before the development of ion-exchange resins, their separation from each other could be achieved only by tedious fractional crystallization or fractional precipitation. Naturally occurring RE separations presumably also take place by these processes. The great difficulties encountered in the laboratory separation and purification of the individual REE considerably confused and delayed their discovery as elements. It is because of their similar behavior that information about both relative and absolute abundances of the REE in "primary" meteoritic and in terrestrial matter is extremely valuable in the establishment of empirical relationships among abundances, nuclear charge, and mass number (SUÈSS and UREY, 1956). Since the REE span an atomic number range from 57 to 71 and a mass number interval from 139 to 176, accurate knowledge of their relative and absolute concentrations will anchor solidly the medium to heavy mass region in any abundance compilation, and will furnish a rigorous test of proposed models for nucleosynthesis.

The difficulties of laboratory separation of the REE seem to have produced on geochemists a firm impression that these elements should constitute an extremely coherent geochemical group, and that their partial separation in nature would occur only in isolated and highly specialized circumstances. Even Goldschmidt, whose careful investigations first revealed the extreme fractionation of this group in minerals (GOLDSCHMIDT and THOMASSEN, 1924), doubted that the relative abundances of the REE in the earth's crust could be different from the primordial distribution for the solar system (GOLDSCHMIDT, 1954). If meteoritic and terrestrial matter originated from the same physicochemical processes in stellar interiors and subsequently condensing nebular matter, then the relative abundances of the REE in meteorites and the earth's crust might very well be expected to be the same. Strong coherence of the RE group has been

the position taken by the authors of the standard textbooks on geochemistry, in many papers, and in some abundance compilations (e. g., RANKAMA and SAHAMA, 1950; GOLDSCHMIDT, 1954; SUÈSS and UREY, 1956; TAYLOR, 1960). This stand is not without justification, for where one of the REE is found in nature, the others are found also. Nevertheless, that fractionations among these elements have occurred during the formation of even the most common kinds of igneous rocks has been undisputedly clear from the time of the earliest RE studies (e. g., VAN TONGEREN, 1938; SAHAMA and VÄHÄTALO, 1941). Recent work has dispelled irrevocably the notion that the REE do not fractionate in nature, and natural RE abundance distributions are beginning to be exploited as a geochemical tool.

The first careful analysis for the REE in meteorites was performed by NODDACK (1935), who used x-ray spectrographic techniques to determine the abundances of these elements in a composite mixture of 12 parts chondrite to 1 part achondrite. In the same year, MINAMI (1935) published x-ray spectrographic measurements of the abundances of the REE in composite samples of three shales. All three shales yielded effectively the same relative RE distribution, and GOLDSCHMIDT (1938) interpreted that abundance pattern to be the average for the earth's crust. Comparison of Minami's shale data with the meteorite values of Noddack showed not only that the REE as a group are much more concentrated in the shales, but also that the lightest REE relative to the heavy REE were up to six times more abundant in the shales than in the meteorites. This unanticipated discrepancy between the relative RE abundances was not generally accepted by geochemists as being real. The x-ray analytical techniques then available were being pushed to their limits of sensitivity, so the differences could be conveniently ascribed to experimental error.

SCHMITT, et al. (1960), determined the RE abundances in two ordinary chondritic meteorites, Allegan and Richardson, by radiochemical neutron activation analysis (RNAA). The relative RE patterns of the two

chondrites were found to agree with those found by NODDACK (1935) to within about  $\pm 30$  per cent. The absolute RE contents were about 6 times lower than those reported by Noddack. By neutron activation analyses of a variety of sedimentary rocks, HASKIN and GEHL (1962) confirmed the correctness of the RE pattern found in shales by MINAMI (1935). The accuracy of the early x-ray spectrographic work of Noddack and Minami attests to their outstanding skill as analysts, for they lacked not only a highly developed x-ray apparatus, but also the sophisticated methods of ion exchange for the separation of pure REE for standards. All subsequent analyses have further substantiated the conclusion that the RE pattern of chondritic meteorites is not the same as that characteristic of the earth's crust.

#### PRESENTATION OF THE DATA

Before the detailed differences between the REE distribution patterns of chondritic meteorites and terrestrial matter can be explored, the problem of how best to compare these patterns must be solved. A number of techniques are in current use, and each is defended by its proponents. Among the simplest is that of splitting the REE into two subgroups, the Ce-earths (La-Gd) and the Y-earths (Tb-Lu, + Y). Gross fractionations can be easily recognized by changes in the abundance ratios of these two subgroups. However, most of the detailed information which is obtained by careful analytical work is lost in such a treatment. Fractionations within a subgroup may be masked, and the enrichment or depletion of Ce and Eu due to mechanisms involving oxidation state changes may not appear, or may produce the impression that all the REE have been fractionated, instead of only one or a few. Variation in the ratio of two elements is also sometimes used to compare REE distribution patterns (e.g., VAINSHTEIN, et al., 1961). An effective ratio should correlate in a definite manner with the separations among the rest of the REE, and no

sufficiently strong correlation exists. Thus, again, some information is lost.

For maximum information, all the RE values must be considered. A method which includes all the elements is to sum the values for the REE, then to determine the per cent of the entire amount that each RE contributes (e.g., MURATA, *et al.*, 1953; MINEYEV, 1963). It is exceedingly difficult to observe other than large differences in RE distributions when comparing two sets of these numbers, and similarities are easily obscured. The method offers little advantage over comparison of the raw analytical data. The technique was used with success by MURATA, *et al.*, (1953), for comparisons of RE patterns for La-Gd from Ce-group minerals because not all the REE were involved and the variation among the patterns was relatively minor. Another method for comparing data involves normalization of all the RE values to the value of one member of the series in order to obviate the effects of differences in absolute abundance and to emphasize the relative distributions (e.g., AHRENS, 1964a; PAVLENKO, VAINSHTEIN, and TURANSKAYA, 1959). Unfortunately, the elements commonly selected for normalization have been La or Nd, both of which are usually fractionated in separation processes, with the result that two closely related RE patterns may yield normalized distributions which appear to be quite different. Yet another technique is to report the ratio of each element to one of its adjacent elements (BALASHOV, 1963c). Trends can be fairly readily observed in this way.

Information concealed in data can often be most rapidly comprehended from graphical displays. This is not the case, however, for simple plots of the type "ppm REE versus atomic number." Figure 1 is such a plot and displays the RE pattern of chondritic meteorites and the average for terrestrial sediments, which happen to be identical for the Y-group (Y-earth group) but different for the Ce-group (Ce-earth group). This can be seen qualitatively by extended and careful scrutiny, but the most

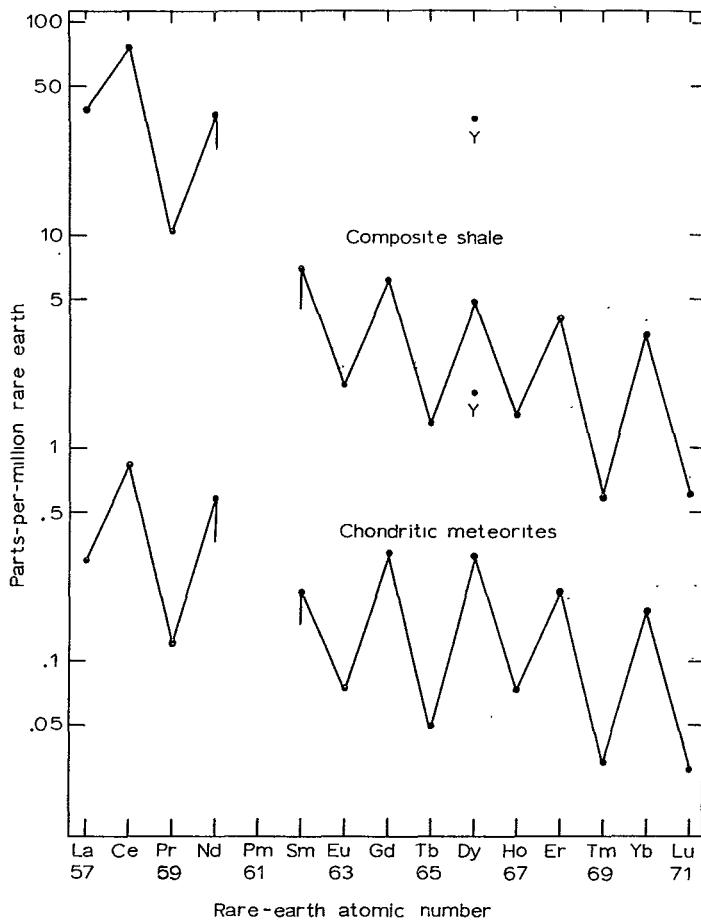


Fig. 1. RE content of the composite of 40 North American shales (Table 28) and average RE content of 20 chondritic meteorites (Table 8), versus RE atomic number. Lower Y value is chondritic value.

striking feature of the plot is the alternation in abundance between adjacent even-Z and odd-Z elements, a classic example of the Oddo-Harkins rule. This problem has been overcome by the use of separate plots for the even-Z and the odd-Z elements (e.g., TAYLOR, 1960).

The procedure used in this paper is to present all the data for two distributions being compared on a single graph. The effects of the Oddo-Harkins rule have been removed by dividing one distribution, element by element, by the other. The resulting ratios have been plotted against atomic number or RE ionic radius (CORYELL, CHASE, and WINCHESTER, 1962; MASUDA, 1962; SCHMITT and SMITH, 1962; CORYELL, CHASE, and WINCHESTER, 1963; HASKIN and GEHL, 1963a; and SCHMITT, et al., 1963). If distributions are identical, all the ratios are the same and a horizontal line results. Trends of differences in the distributions appear as curves or sloped lines. In most cases, the differences in absolute RE abundance have been reduced as well, by normalization of each distribution to its Yb content. Yb is a superior element for normalization because it can be determined accurately by the principal methods currently in use, and because the extent of fractionation among the heaviest REE in most of the systems analyzed is small. The use of the average of the Eu, Gd, and Tb contents as a normalization standard has been proposed (JENSEN and BRUNFELD, 1965), especially since older analytical results often do not include values for the heavy REE. However, Eu contents are anomalously variable, and Gd and Tb are not as precisely determinable as Yb by neutron activation analysis, so the use of these elements for normalization is not recommended.

Ionic radius is used as the abscissa for the abundance plots in this paper, as it is a meaningful chemical parameter which might be expected to influence the fractionation of the REE. This choice is quite arbitrary and may be no better than the use of atomic number for the abscissa, especially since it has been shown (MASUDA, 1963c) that the reciprocals

of the lanthanide ionic radii are a linear function of atomic number. The ionic radius of Y is similar to that of Dy, and its geochemical behavior is extremely close to that of the heavier lanthanides. Values for Y are plotted close to those for Dy, or in place of those for Dy when no Dy value was reported. The values used for the ionic radii are those of AHRENS (1952).

The data of Fig. 1 have been treated as specified above, and are plotted in Fig. 2. It is readily apparent that the average RE pattern for terrestrial sediments is identical to that of chondritic meteorites for the elements Gd-Lu, but the sediments are relatively enriched in the light REE, with a smooth increase in enrichment from Eu to La.

Nearly all the RE patterns displayed in this paper have been divided by the pattern found in chondritic meteorites. This is a matter of convenience, and is not intended to imply a close genetic relationship between a particular rock sample and chondrites unless specifically stated. In most of the figures, a line representing the average sediment pattern has been included so that rapid comparisons of the RE pattern being considered with both the meteoritic and crustal patterns can be made.

Most of the recent x-ray spectrographic and neutron-activation data reported are accurate to about  $\pm 5$  to 10 per cent. Error bars in the figures indicate standard deviations for the element ratios. These uncertainties were calculated from the exact reported standard deviations for RE data when they were given, and were estimated from the above range when they were not.

This review paper represents an attempt to present and evaluate the available RE abundance data up to the fall of 1965. Emphasis is placed on correlations among meteoritic, solar, and terrestrial matter. Whole-rock distributions are stressed, and information on RE minerals is condensed. Interpretation of the RE patterns must necessarily be brief, and those interested are referred to the indicated references for detailed or extended arguments.

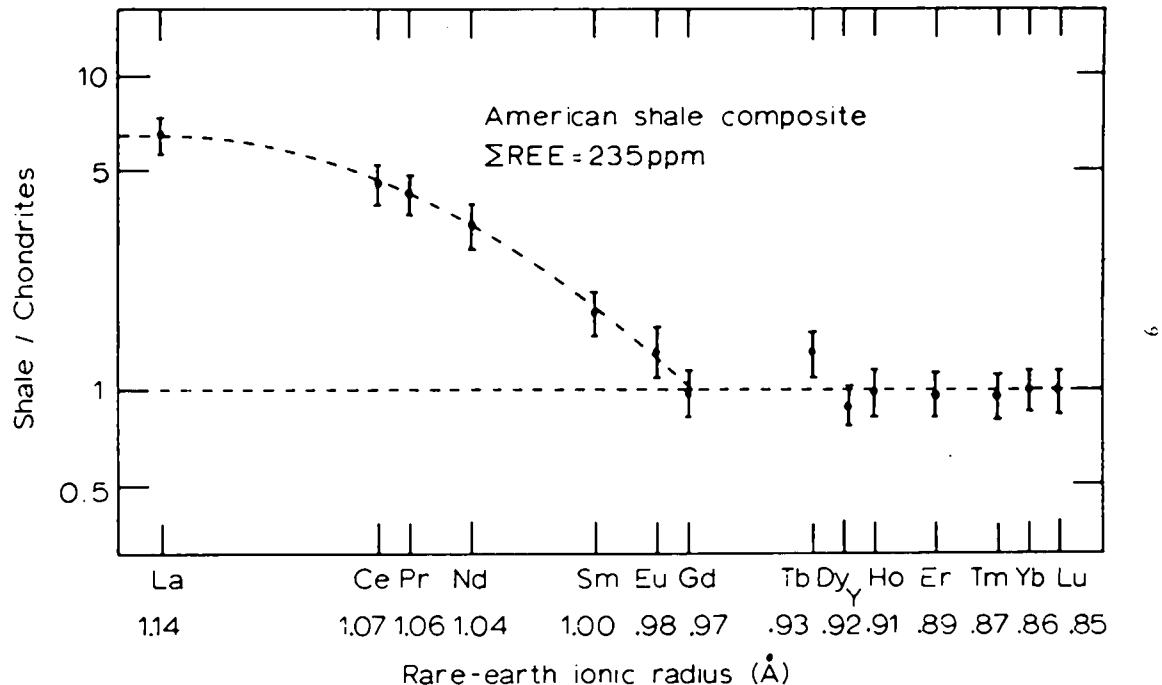


Fig. 2. - Comparison plot for the North American shale composite. The ppm REE in the shales have been normalized to  $\text{Yb} = 1.00$ , then divided, element by element, by the Yb-normalized average for chondritic meteorites. The resulting ratios have been plotted on a logarithmic scale against RE ionic radius. The two RE distributions are identical for Gd-Lu, whose ratios lie along a horizontal line. The increasing relative enrichment of the shales in the elements Sm-La shows up clearly.

## REE IN METEORITIC MATTER

In this paper, emphasis has been placed on the abundances of the REE and Sc in chondritic (or ordinary stony) meteorites because the chondritic meteorites are considered by UREY (1952) to be the best (available) representative samples in the solar system of the abundances of the nonvolatile elements. Abundances of the REE and Sc in chondritic matter will be referred to as "primordial."

Very briefly, chondritic meteorites comprise about 86 per cent of all observed meteoritic falls (MASON, 1962). Small siliceous chondrules, or spheroidal bodies ( $\sim$ 1 mm diameter), are scattered throughout the stony chondrites. The chondrites have been classified into five categories, according to gradual changes in their chemical and mineralogical composition: Types I, II, and III carbonaceous chondrites; high-iron (H-group) chondrites; low-iron (L-group) chondrites; Soko-Banjitic (LL-group) chondrites; and enstatitic chondrites.

Achondritic (stony) meteorites, about 8 per cent of observed falls, lack chondrules and differ from chondrites primarily in having greater coarseness in crystallinity and a heterogeneous chemical and mineralogical composition, which approximates that of terrestrial rocks in some cases. Achondrites are divided into two principal groups: (1) the Ca-rich achondrites ( $\sim$ 10 per cent Ca concentration), with the eucrites and howardites as one subgroup and the nakhlites as another subgroup; and (2) the Ca-poor achondrites ( $\sim$ 2 per cent Ca concentration). Other meteoritic types, which account for the remaining  $\sim$ 6 per cent of observed falls, are iron meteorites and stony-iron meteorites such as pallasites and mesosiderites. The latter two consist of  $\sim$ 50 per cent metallic and  $\sim$ 50 per cent silicate phases.

REE and Sc abundances in 20 chondritic meteorites were obtained by the accurate technique of RNAA (radiochemical neutron activation analysis) (whole rock type) and are summarized in Tables 1 and 2. References where details of these results may be found are given in footnotes to Table 1. The general RNAA method of MOSEN, SCHMITT, and VASILEVSKIS (1961), with modifications noted by SCHMITT, et al. (1963), was used for most of this work.

In this procedure, the activated REE and Sc are separated individually by standard chromatographic ion-exchange techniques. Recently, LUKENS and GRABER (1965) have modified and simplified this RNAA technique. Their procedure essentially consists of radiochemical separation of the REE and Sc as a group from the silicate matrix, followed by gamma ray spectroscopy on the composite mixture of activated REE and Sc. For terrestrial silicates, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Sc may be measured accurately by their technique.

In general, about 5 g of meteoritic matter were subjected to RNAA. Analysis of 5-g specimens usually is dictated by the fact that only small quantities of meteorites are available for any particular research in these elemental analyses. Such small masses represent  $\sim 0.1$  to 1 percent of the total mass of the average chondritic or achondritic stony meteorite. For other meteorites, such as pallasites, mesosiderites, and iron meteorites, an analyzed specimen of  $\sim 5$  g may represent  $\sim 10^{-5}$  to 1 per cent of the total mass. Observed abundances must thus always be treated within the restriction of the small specimen fractions employed.

All except one of the chondritic meteorites included in Tables 1 and 2 were analyzed by SCHMITT, et al. (1963); SCHMITT, SMITH, and OLEHY (1964); and SCHMITT and SMITH (1963b). The chondrite Forest City (Table 2) was analyzed by HASKIN and GEHL (1962). In Table 3, absolute abundances of the REE and Sc are given for four Ca-rich eucritic achondrites, two mesosiderites, two nakhrites, and three Ca-poor achondrites (one enstatitic and two hyperstheneic) (SCHMITT, et al., 1963;

Table 1. Absolute Abundances of REE and Sc in Carbonaceous Chondritic Meteorites as Determined by NAA<sup>a</sup>  
(Abundances in  $10^{-6}$  g/g of Sample (ppm))

Element	Isotope Measured	Radio-nuclide	Type I		Type II			Type III		
			Ivuna	Orgueil	Boriskino	Mghei	Murray	Felix	Groznaiia	Mokoia
La	La <sup>139</sup>	40-h La <sup>140</sup>	0.19±0.01	0.19±0.01	0.25±0.01	0.29±0.01	0.39±0.02	0.34±0.01	0.38±0.02	0.46±0.01
Ce	Ce <sup>140</sup>	32-d Ce <sup>141</sup>	0.60±0.01	0.66±0.01	0.94±0.03	0.76±0.02	1.09±0.06	----	1.25±0.02	----
	Ce <sup>142</sup>	33-h Ce <sup>143</sup>	0.57±0.01	0.67±0.01	0.94±0.09	0.71±0.01	1.00±0.12	1.08±0.02	1.22±0.02	1.06±0.02
Pr	Pr <sup>141</sup>	19-h Pr <sup>142</sup>	0.090±0.003	0.097±0.001	0.094±0.005	0.13±0.01	0.15±0.01	0.14±0.02	0.13±0.01	0.16±0.01
Nd	Nd <sup>146</sup>	11.6-d Nd <sup>147</sup>	0.40±0.02	0.44±0.03	0.57±0.06	0.61±0.04	0.62±0.04	0.81±0.12	0.80±0.04	0.84±0.02
Sm	Sm <sup>152</sup>	47-h Sm <sup>153</sup>	0.134±0.003	0.131±0.002	0.19±0.01	0.20±0.01	0.21±0.01	0.28±0.01	0.27±0.01	0.31±0.01
Eu	Eu <sup>151</sup>	9.3-h Eu <sup>152m</sup>	0.053±0.002	0.047±0.002	0.071±0.002	0.078±0.001	0.073±0.004	0.105±0.003	0.097±0.003	0.102±0.003
	Eu <sup>151</sup>	13-y Eu <sup>152</sup>	0.057±0.002	0.053±0.002	0.073±0.002	0.077±0.003	0.071±0.002	0.096±0.003	0.097±0.004	0.103±0.004
Gd	Gd <sup>158</sup>	1.8-h Gd <sup>159</sup>	0.24±0.04	----	0.30±0.02	0.38±0.02	0.27±0.03	0.40±0.04	0.46±0.02	0.40±0.02
	Gd <sup>160</sup>	7.0-d Tb <sup>161</sup>	----	----	----	----	0.28±0.02	----	----	----
Tb	Tb <sup>159</sup>	72-d Tb <sup>160</sup>	0.066±0.003	0.022±0.002	0.041±0.003	0.047±0.002	0.049±0.005	0.061±0.001	0.057±0.003	0.073±0.002
Dy	Dy <sup>164</sup>	2.3-h Dy <sup>165</sup>	----	0.22±0.01	----	0.36±0.07	0.32±0.02	----	0.39±0.02	0.42±0.03
Ho	Ho <sup>165</sup>	27.5-h Ho <sup>166</sup>	0.058±0.001	0.054±0.001	0.062±0.001	0.076±0.002	0.079±0.004	0.096±0.002	0.086±0.002	0.098±0.003
Er	Er <sup>168</sup>	9.4-d Er <sup>169</sup>	0.146±0.005	0.15±0.010	0.29±0.02	0.24±0.02	0.24±0.01	0.27±0.01	0.23±0.01	0.25±0.01
	Er <sup>170</sup>	7.5-h Er <sup>171</sup>	0.15±0.014	0.113±0.009	0.22±0.01	0.17±0.01	0.21±0.01	0.29±0.01	0.24±0.01	0.27±0.01
Tm	Tm <sup>169</sup>	129-d Tm <sup>170</sup>	0.022±0.002	0.022±0.004	0.031±0.004	0.030±0.004	0.037±0.002	0.037±0.003	0.038±0.006	0.047±0.004
Yb	Yb <sup>168</sup>	32-d Yb <sup>169</sup>	0.103±0.002	0.14±0.01	0.18±0.01	0.17±0.01	0.17±0.01	0.19±0.01	0.21±0.01	0.24±0.01
	Yb <sup>174</sup>	4.2-d Yb <sup>175</sup>	0.122±0.003	0.17±0.01	0.17±0.01	0.17±0.01	0.19±0.01	0.20±0.01	0.22±0.01	0.25±0.01
Lu	Lu <sup>175</sup>	7.5-h Lu <sup>176</sup>	----	----	----	----	----	----	----	----
	Lu <sup>176</sup>	6.8-d Lu <sup>177</sup>	0.024±0.003	0.022±0.001	0.027±0.001	0.032±0.005	0.030±0.002	0.037±0.001	0.034±0.001	0.038±0.001
Y	Y <sup>89</sup>	64-h Y <sup>90</sup>	1.7±0.2	1.4±0.2	2.1±0.1	1.8±0.2	----	2.4±0.1	2.4±0.2	2.4±0.1
Sc	Sc <sup>45</sup>	85-d Sc <sup>46</sup>	5.9±0.3	5.3±0.2	8.1±0.2	8.6±0.2	11.3±0.2	9.7±0.3	10.1±0.2	10.4±0.2
ΣREE			3.8	3.6	5.5	5.1	5.5	6.3	6.8	6.9

<sup>a</sup> Values for elemental abundances were calculated by assuming that terrestrial and meteoritic isotopic ratios were identical for all REE. This assumption has been verified for five REE isotopic ratios and particularly for the Yb<sup>168</sup>/Yb<sup>174</sup> ratio, which is strongly dependent on differing types of nucleosynthesis for these two isotopes. MURTHY and SCHMITT (1963) have identified to ±0.5 per cent several critical REE isotopic ratios in terrestrial and meteoritic matter. Errors are primarily one standard deviation due to counting statistics. The chondrites are classified after DON (1962).

Table 2. Absolute Abundances of REE and Sc in Ordinary, Sokó-Banjite, and Enstatitic Chondrites as Determined by NAA<sup>a</sup>  
(Abundances in  $10^{-6}$  g/g of Sample (ppm))

Element	Isotope <sup>b</sup> Measured	Ordinary Chondrites							Sokó-Banjites			Enstatites		
		H-group				L-group			Manhhoom		Vavilovka	Abec	Indarch	St. Marks
		Allegan	Forest City	Miller	Richardton	Holbrook	Kyushu	Modoc						
La	La <sup>139</sup>	0.33±0.02	0.33±0.02	0.29±0.01	0.32±0.02	0.45±0.02	0.30±0.01	0.34±0.01	0.31±0.01	0.25±0.01	0.15±0.01	0.21±0.01	0.25±0.01	
Ce	Ce <sup>140</sup>	0.54±0.04	----	----	----	2.1±0.1	----	1.42±0.03	0.87±0.01	0.88±0.01	----	----	0.68±0.03	
	Ce <sup>142</sup>	0.54±0.04	----	0.88±0.02	0.48±0.05	2.2±0.1	0.92±0.03	1.6±0.1	0.94±0.01	0.84±0.01	0.48±0.01	0.59±0.01	0.64±0.05	
Pr	Pr <sup>141</sup>	0.12±0.01	0.12±0.01	0.13±0.01	0.12±0.01	0.16±0.01	0.13±0.01	0.13±0.01	0.12±0.01	0.075±0.008	0.054±0.001	0.11±0.01	0.13±0.01	
Nd	Nd <sup>146</sup>	0.65±0.11	0.62±0.03	0.52±0.03	0.61±0.05	0.79±0.01	0.57±0.01	0.63±0.02	0.65±0.005	0.076±0.003(out)	0.24±0.01	0.37±0.02	0.36±0.01	
Sm	Sm <sup>152</sup>	0.24±0.01	0.22±0.01	0.20±0.01	0.20±0.01	0.28±0.01	0.22±0.01	0.20±0.01	0.24±0.003	0.190±0.004	0.095±0.002	0.14±0.01	0.14±0.01	
Eu	Eu <sup>151m</sup>	0.091±0.004	0.088±0.004	----	0.081±0.004	0.090±0.001	0.084±0.003	0.076±0.002	0.077±0.002	0.067±0.002	0.045±0.002	0.043±0.002	0.044±0.002	
	Eu <sup>151</sup>	0.083±0.004	----	0.066±0.002	0.079±0.004	0.095±0.003	0.075±0.002	0.084±0.005	0.081±0.001	----	0.054±0.004	0.041±0.002	0.046±0.001	
Gd	Gd <sup>158</sup>	0.34±0.03	0.40±0.02	0.29±0.02	0.28±0.06	0.43±0.01	0.36±0.01	0.33±0.01	0.26±0.01	0.31±0.05	0.16±0.01	0.21±0.01	0.18±0.01	
	Gd <sup>160</sup>	0.34±0.03	----	----	0.40±0.03	0.35±0.02	----	----	----	----	----	----	0.23±0.02	
Tb	Tb <sup>159</sup>	0.049±0.004	0.057±0.003	0.052±0.002	0.053±0.003	0.068±0.003	0.044±0.002	0.048±0.001	0.059±0.001	0.046±0.003	0.025±0.001	0.031±0.001	0.036±0.002	
Dy	Dy <sup>164</sup>	0.39±0.02	----	0.26±0.01	0.34±0.02	0.42±0.01	0.26±0.01	0.30±0.02	0.35±0.02	0.32±0.03	0.16±0.02	0.18±0.02	0.21±0.02	
Ho	Ho <sup>165</sup>	0.082±0.007	0.068±0.003	0.074±0.001	0.068±0.009	0.103±0.002	0.068±0.001	0.084±0.002	0.089±0.002	0.066±0.001	0.040±0.001	0.053±0.001	0.046±0.003	
Er	Er <sup>168</sup>	----	0.25±0.02	----	0.20±0.03	0.33±0.01	0.22±0.01	----	0.23±0.02	0.17±0.02	0.15±0.01	----	----	
	Er <sup>170</sup>	0.22±0.03	----	0.22±0.01	0.21±0.01	0.29±0.01	0.21±0.01	0.23±0.01	0.25±0.01	0.162±0.013	0.131±0.093	0.15±0.01	0.14±0.01	
Tm	Tm <sup>169</sup>	0.043±0.004	0.053±0.002	0.027±0.002	0.033±0.002	0.043±0.002	0.030±0.001	0.033±0.002	0.036±0.002	0.032±0.004	0.014±0.001	0.023±0.003	0.024±0.002	
	Yb <sup>168</sup>	0.20±0.05	----	----	0.19±0.01	0.22±0.01	0.20±0.01	0.135±0.004	0.21±0.01	----	----	0.121±0.003	0.134±0.005	
	Yb <sup>174</sup>	0.19±0.02	0.19±0.01	0.17±0.01	0.19±0.02	0.24±0.01	0.22±0.01	0.16±0.01	0.18±0.01	0.16±0.01	0.094±0.002	0.124±0.003	0.135±0.003	
Lu	Lu <sup>175</sup>	0.035±0.007	----	----	----	----	----	----	----	----	----	----	----	
	Lu <sup>176</sup>	0.041±0.004	----	0.030±0.001	0.033±0.002	0.037±0.001	0.035±0.001	0.036±0.001	0.033±0.001	0.029±0.001	0.019±0.001	0.023±0.001	0.027±0.001	
Y	Y <sup>89</sup>	----	2.2±0.1	2.1±0.1	----	----	2.0±0.1	2.1±0.1	2.0±0.1	1.9±0.1	1.02±0.06	1.5±0.1	----	
Sc	Sc <sup>45</sup>	----	----	----	----	~8.2	8.5±0.2	8.1±0.2	8.8±0.1	----	5.3±0.1	7.2±0.2	----	
REEE		5.3	4.6	5.3	5.6	5.5	5.4	7.5	5.5	4.6	2.7	3.7	3.8	

<sup>a</sup> See footnote a of Table 1.

<sup>b</sup> Resultant radionuclides are given in column 3 of Table 1.

Table 3. Absolute Abundances of REE and Sc in Ca-rich and Ca-poor Achondrites as Determined by NAA<sup>a</sup>  
 (Abundances in  $10^{-6}$  g/g Sample (ppm))

Element	Isotope <sup>b</sup> Measured	Ca-rich Achondrites								Ca-poor Achondrites		
		Euclites (Pyroxene plagioclase)				Mesosiderites (Pyroxene-plagioclase silicates)		Nakhlites (Diopside-olivine)		Enstatites (Aubrites)	Hypersthene Diogenites	
		Juvina	Nuevo Laredo	Pasamonte	Stannern	Estherville (Silicate Phase)	Veranum (Silicate Phase)	Lafayette	Nakhla		Johnstown	Shalaka
La	La <sup>139</sup>	2.5±0.1	4.0±0.1	3.2±0.1	4.9±0.1	1.1240.03	0.2940.01	1.8±0.1	1.6±0.1	0.21±0.01	0.044±0.002	0.015±0.001
Ce	Ce <sup>140</sup>	7.340.2	10.4±0.5	8.6±0.2	12.6±0.2	-----	0.82±0.02	5.5±0.2	6.0±0.1	-----	-----	-----
Ce	Ce <sup>142</sup>	7.2±0.2	11.0±0.6	7.6±0.2	13.2±0.2	3.040.1	0.91±0.03	5.5±0.1	6.4±0.2	0.81±0.02	-----	-----
Pr	Pr <sup>141</sup>	0.9840.03	1.4740.05	1.26±0.03	2.0±0.1	0.37±0.02	0.114±0.005	0.80±0.03	0.67±0.03	0.11±0.01	-----	0.0062±0.0006
Nd	Nd <sup>146</sup>	5.0±0.1	8.4±0.3	5.7±0.1	10.0±0.2	2.1±0.1	0.57±0.07	3.4±0.1	3.2±0.2	0.63±0.01	-----	-----
Nd	Nd <sup>150</sup>	-----	7.6±0.7	4.5±0.1	-----	-----	-----	-----	-----	-----	-----	-----
Sm	Sm <sup>152</sup>	1.7±0.1	2.240.1	1.9±0.1	3.2±0.1	0.68±0.01	0.23±0.01	0.85±0.02	0.73±0.02	0.22±0.01	0.080±0.002	0.0103±0.0003
Eu	Eu <sup>151</sup>	0.60±0.02	0.75±0.07	0.67±0.01	0.8640.02	0.2240.01	0.113±0.002	0.2440.01	0.20±0.01	-----	0.0089±0.0002	0.003740.0002
Eu	Eu <sup>151</sup>	0.64±0.02	0.74±0.01	0.69±0.01	0.80±0.03	0.21±0.01	0.122±0.005	0.23±0.01	0.19±0.01	0.022±0.001	0.0089±0.0007	0.0043±0.0003
Gd	Gd <sup>158</sup>	2.6±0.1	2.44±0.2	2.7±0.1	4.5±0.1	1.1040.03	0.44±0.02	0.92±0.04	0.94±0.03	0.38±0.02	-----	-----
Gd	Gd <sup>160</sup>	-----	2.54±0.2	-----	-----	-----	-----	-----	-----	-----	-----	-----
Tb	Tb <sup>159</sup>	0.40±0.01	0.59	-----	0.71±0.02	0.14±0.01	0.054±0.004	0.120±0.003	0.109±0.002	0.061±0.004	-----	-----
Dy	Dy <sup>164</sup>	3.0±0.1	4.1±0.2	3.1±0.1	4.9±0.1	0.97±0.04	0.37±0.01	0.89±0.14	-----	0.40±0.17	0.14.0.01	-----
Ho	Ho <sup>165</sup>	0.59±0.01	0.84±0.02	0.69±0.04	1.07±0.03	0.23±0.01	0.097±0.002	0.146±0.004	0.140±0.002	0.100±0.004	0.036±0.001	0.0046±0.0003
Er	Er <sup>168</sup>	1.7±0.1	3.1±0.2	1.7±0.3	3.0±0.2	0.60±0.01	0.27±0.03	0.47±0.03	0.36±0.02	0.25±0.01	-----	-----
Er	Er <sup>170</sup>	1.94±0.1	2.6±0.2	1.6±0.1	3.1±0.1	0.65±0.01	0.25±0.01	0.40±0.01	0.32±0.01	-----	0.14±0.01	0.021±0.003
Tm	Tm <sup>169</sup>	0.28±0.01	0.48±0.04	0.30±0.02	0.47±0.02	0.096±0.010	0.041±0.005	0.047±0.003	0.057±0.006	0.036±0.001	0.021±0.002	0.003740.0001
Yb	Yb <sup>168</sup>	1.37±0.04	2.5±0.3	1.6±0.1	2.4±0.1	0.48±0.01	0.19±0.01	0.21±0.01	0.28±0.02	0.21±0.01	-----	-----
Yb	Yb <sup>174</sup>	1.37±0.04	2.2±0.3	1.7±0.1	2.4±0.1	0.52±0.01	0.23±0.01	0.24±0.01	0.36±0.01	0.23±0.01	0.15±0.01	0.024±0.001
Lu	Lu <sup>175</sup>	-----	-----	0.60±0.06	-----	-----	-----	-----	-----	-----	-----	-----
Lu	Lu <sup>176</sup>	0.23±0.01	0.30±0.05	0.40±0.06	0.38±0.01	0.083±0.001	0.044±0.002	0.044±0.001	0.051±0.002	0.039±0.001	0.033±0.001	0.0058±0.0001
Y	Y <sup>89</sup>	17±0.3	-----	-----	28±1	5.6±0.2	2.5±0.2	3.2±0.2	4.4±0.2	2.09±0.16	1.22±0.06	0.22±0.02
Sc	Sc <sup>45</sup>	28±1	43±2	39±1	31±1	18±1	16±1	54±1	78±2	9.0±0.2	14.0±0.2	9.8±0.2
ZREE		46	65	48	79	17	6.2	19	19	5.6	1.9	0.31

<sup>a</sup>See footnote a of Table 1.

<sup>b</sup>See footnote b of Table 2.

SCHMITT, SMITH, and OLEHY, 1964). Table 4 lists absolute RE and Sc abundances in the olivine phases of two pallasites and in two iron meteorites.

In Tables 1 and 2, the first two columns contain the individual REE and Sc and the isotopes that were activated during neutron activation. The radioactivities of the radionuclides given in column 3 of Table 1 were counted by appropriate scintillation or beta-ray spectrometric techniques in order to calculate the abundances of the respective elements. Standard deviations ( $\pm$  values) listed after all the abundances are principally due to counting statistics. Other possible errors, such as in weighing and counting geometries, are normally less than a few per cent.

In order to compare the RE and Sc abundances among the various meteoritic categories and types, normalized abundances relative to Yb at 1.00 are presented in Tables 5 and 6. The early x-ray spectroscopic work of NODDACK (1935) has also been normalized to Yb at 1.00, and appears in the last column of Table 5. In these two tables, the mean deviations from the arithmetic mean of normalized values are given as ( $\pm$ ) values.

In Table 7, the atomic abundances of La and Yb, two representative lanthanides, and also of Y and Sc have been calculated relative to  $10^6$  Si atoms for the different kinds of chondritic meteorites.

In Table 8, a summary of absolute average mass abundances (in ppm), with the associated mean deviation and atomic abundances relative to  $10^6$  Si atoms, is given. To permit comparison with current nucleosynthetic theory, column 4 gives the normalized atomic abundances in 20 chondritic meteorites, and column 5 gives the normalized theoretical abundances after CLAYTON, et al. (1961), and CLAYTON and FOWLER (1961). Average abundances of the REE and Sc in four eucritic Ca-rich achondrites are given in column 6, and the ratio of the averages in these achondrites to the respective average abundances in 20 chondritic meteorites is given in the last column.

Table 4. Absolute Abundances of REE and Sc in Pallasitic and Iron Meteorites as Determined by NAA<sup>a</sup>  
(Abundances given in  $10^{-6}$  g/g Sample (ppm))

Element	Isotope <sup>b</sup> Measured	Pallasites		Irons	
		Brenham (Olivine Phase)	Thiel Mts. (Olivine Phase)	Aroos	Odessa
La	La <sup>139</sup>	----	0.12±0.01	$(4.1\pm0.4)\times10^{-4}$	----
Ce	Ce <sup>140</sup>	----	----	----	----
	Ce <sup>142</sup>	$<0.17\pm0.01$	0.28±0.03	----	----
Pr	Pr <sup>141</sup>	0.032±0.002	0.022±0.001	$(1.9\pm0.2)\times10^{-4}$	----
Nd	Nd <sup>146</sup>	0.16±0.01	0.12±0.01	----	----
Sm	Sm <sup>152</sup>	0.112±0.002	0.022±0.001	$(79\pm6)\times10^{-6}$	$(36\pm4)\times10^{-6}$
Eu	Eu <sup>151m</sup>	0.018±0.001	0.0031±0.0001	$(27\pm3)\times10^{-6}$	$(12\pm1)\times10^{-6}$
	Eu <sup>151</sup>	0.017±0.001	----	----	----
Gd	Gd <sup>158</sup>	----	0.020±0.003	----	----
Tb	Tb <sup>159</sup>	0.038±0.002	----	----	----
Dy	Dy <sup>164</sup>	----	0.016±0.003	$(1.5\pm0.2)\times10^{-4}$	----
Ho	Ho <sup>165</sup>	0.051±0.002	0.0034±0.0002	$<(4.2\pm0.4)\times10^{-4}$	$<(10\pm3)\times10^{-6}$
Er	Er <sup>168</sup>	0.097±0.006	----	----	----
	Er <sup>170</sup>	0.091±0.004	----	----	----
Tm	Tm <sup>169</sup>	0.0096±0.0009	0.0010±0.0002	----	----
Yb	Yb <sup>174</sup>	0.043±0.001	0.0086±0.0005	----	----
Lu	Lu <sup>176</sup>	0.0059±0.0004	0.0017±0.0002	----	----
Y	Y <sup>89</sup>	1.6±0.2	----	----	----
Sc	Sc <sup>45</sup>	0.79±0.03	1.15±0.02	----	----
$\Sigma$ REE		~2, 3	0.72		

<sup>a</sup> See footnote a of Table 1.

<sup>b</sup> See footnote b of Table 2.

Table 5. Normalized Abundances of REE and Sc in Chondritic Meteorites<sup>a</sup>

Element	Avg. in 2 Type I Carbonaceous Chondrites	Avg. in 3 Type II Carbonaceous Chondrites	Avg. in 3 Type III Carbonaceous Pigeonitic Chondrites	Avg. in 4 H-group Chondrites	Avg. in 3 L-group Chondrites	Avg. in 2 Sokol-Banjites	Avg. in 3 Enstatites	Avg. in 20 Chondrites	Avg. in 12 Parts Chondrite to 1 Part Ca-rich Achondrite (NODDACK, 1935)
La	1.44±0.22	1.83±0.26	1.77±0.05	1.72±0.03	1.87±0.29	1.57±0.02	1.73±0.09	1.72±0.17	1.11
Ce	4.27-5.14	5.05-5.72	4.19-5.60	5.15 <sup>b</sup>	4.4-9.8	4.46-5.35	4.89-5.11	5.02±0.40 <sup>c</sup>	1.24
Pr	0.70±0.08	0.74±0.13	0.65±0.04	0.68±0.05	0.72±0.08	0.55±0.08	0.81±0.16	0.70±0.11	0.52
Nd	3.16±0.34	3.57±0.31	3.72±0.32	3.27±0.14	3.42±0.48	3.34	2.76±0.22	3.32±0.34	1.82
Sm	1.01±0.17	1.19±0.12	1.29±0.10	1.18±0.07	1.19±0.10	1.22±0.03	1.08±0.07	1.17±0.09	0.67
Eu	0.40±0.08	0.45±0.05	0.46±0.05	0.43±0.03	0.44±0.06	0.43±0.03	0.40±0.08	0.43±0.05	0.17
Gd	2.10	1.92±0.40	1.91±0.22	1.85±0.12	1.86±0.20	1.63±0.30	1.67±0.10	1.84±0.22	1.00
Tb	0.36±0.21	0.27±0.03	0.29±0.03	0.30±0.02	0.27±0.04	0.29±0.01	0.26±0.01	0.29±0.04	0.31
Dy	1.42	2.06±0.32	1.71±0.07	1.81±0.20	1.68±0.28	1.90±0.10	1.59±0.07	1.75±0.20	1.27
Ho	0.43±0.09	0.43±0.05	0.42±0.04	0.40±0.04	0.45±0.08	0.43±0.03	0.40±0.05	0.42±0.05	0.35
Er	1.07±0.24	1.36±0.09	1.20±0.19	1.22±0.08	1.29±0.19	1.16±0.13	1.22±0.12	1.23±0.15	1.05
Tm	0.167±0.025	0.193±0.009	0.183±0.007	0.181±0.022 <sup>d</sup>	0.182±0.026	0.185±0.002	0.173±0.016	0.181±0.017 <sup>d</sup>	0.19
Yb	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Lu	0.176±0.034	0.178±0.023	0.166±0.017	0.180±0.010	0.188±0.032	0.181±0.006	0.199±0.004	0.181±0.021	0.33
Y	12.0±2.8	11.9±0.3	11.0±1.0	11.8±0.5	11.5±2.1	11.1±0.9	11.6±0.7	11.5±1.2	----
Sc	43±9	55±6	46±3	----	43±7	48±4	49±5	47±6	----

<sup>a</sup>Data of Tables 1 and 2 normalized to Yb at 1.00.<sup>b</sup>Allegan and Richardson excluded.<sup>c</sup>Allegan, Richardson, Holbrook, Modoc, and Forest City excluded.<sup>d</sup>Forest City excluded.

Table 6. Normalized Abundances of REE and Sc in  
Ca-rich Achondrites

Element	Average in 4 Eucrites	Average in 2 Nakhrites
La	1.89±0.11	6.2±0.8
Ce	5.06±0.34	22.4±5.2
Pr	0.73±0.06	2.74±0.27
Nd	3.73±0.27	12.2±1.8
Sm	1.17±0.14	2.96±0.32
Eu	0.39±0.04	0.80±0.07
Gd	1.62±0.28	3.53±0.77
Tb	0.28±0.02 <sup>a</sup>	0.42±0.06
Dy	1.98±0.17	2.80 <sup>b</sup>
Ho	0.42±0.03	0.54±0.08
Er	1.20±0.11	1.43±0.08
Tm	0.198±0.009	0.193±0.017
Yb	1.00	1.00
Lu	0.154±0.016 <sup>a</sup>	0.175±0.021
Y	12.2±0.4 <sup>c</sup>	13.9±0.2
Sc	19±3	240±2

<sup>a</sup>Pasamonte excluded.

<sup>b</sup>Nakhla excluded.

<sup>c</sup>Nuevo Laredo and Pasamonte excluded.

Table 7. Atomic Abundances, Relative to  $10^6$  Si Atoms, of La and Yb (Representative REE) and Y and Sc in Various Kinds of Chondritic Meteorites<sup>a</sup>

	Carbonaceous			Ordinary		Soko-Banjitic	Enstatitic
	Type I	Type II	Type III	H-group	L-group		
La	$0.36 \pm 0.01$	$0.47 \pm 0.08$	$0.51 \pm 0.05$	$0.38 \pm 0.02$	$0.39 \pm 0.06$	$0.30 \pm 0.03$	$0.22 \pm 0.03$
	$0.43 \pm 0.01^b$						
Yb	$0.21 \pm 0.03$	$0.21 \pm 0.01$	$0.22 \pm 0.02$	$0.18 \pm 0.01$	$0.17 \pm 0.02$	$0.15 \pm 0.02$	$0.10 \pm 0.01$
Y	$4.8 \pm 0.4$	$4.6 \pm 0.4$	$4.9 \pm 0.2$	$3.9 \pm 0.2$	$3.4 \pm 0.2$	$3.2 \pm 0.1$	$2.1 \pm 0.4$
Sc <sup>c</sup>	$34 \pm 2$	$44 \pm 6$	$41 \pm 1$	-----	$28 \pm 1$	$29 \pm 1$	$21 \pm 3$
	$(32 \pm 1)^2$	$(35 \pm 4)^7$	$(41 \pm 10)^5$	$(31 \pm 4)^{20}$	$(29 \pm 3)^{29}$	$(26 \pm 1)^{10}$	$(26 \pm 6)^4$

<sup>a</sup> Average Si abundances used in these calculations from data of Tables 1 and 2 were Type I, 10.4 per cent Si; Type II, 13.3 per cent Si; Type III, 15.4 per cent Si (MASON, 1962-1963); H-group, 17.1 per cent Si; L-group, 18.6 per cent Si (CRAIG, 1964); Soko-Banjitic, 18.8 per cent (MASON and WIILK, 1964); and enstatitic, 18.4 per cent Si (UREY and CRAIG, 1953).

<sup>b</sup> Atomic value obtained assuming La had been fractionated by 16 per cent. See text for details.

<sup>c</sup> Sc values not in parentheses were calculated from the data in Tables 1 and 2. Sc values in parentheses are average concentrations determined by INAA by SCHMITT and SMITH (1964a) and SCHMITT, GOLES, and SMITH (1966), with the number of meteorites for each type of chondrites being listed by superscripts.

Table 8. Summary of Mass and Atomic Abundances of REE and Sc in 20 Chondritic and 4 Ca-rich Achondritic Meteorites<sup>a</sup>

Element	20 Chondrites				4 Achondrites (Euclites)	
	Average Absolute Mass Abundance (ppm)	Average Atomic Abundance (atoms/10 <sup>6</sup> Si atoms) <sup>b</sup>	Normalized Atomic Abundance <sup>c</sup>	Normalized Calculated Atomic Abundance <sup>d</sup>	Average Absolute Mass Abundance (ppm) <sup>e</sup>	Abundance Ratio <sup>f</sup> <u>Euclitic Achondrites</u> Chondrites
La	0.30±0.06	0.38	2.2	1.9	3.7±0.8	12.3
Ce	0.84±0.18 <sup>g</sup>	1.05	6.2	3.1	9.7±2.1	11.6
Pr	0.12±0.02	0.15	0.88	0.44	1.4±0.3	11.7
Nd	0.58±0.13	0.71	4.2	2.1	7.0±2.0	12.1
Sm	0.21±0.04	0.24	1.4	1.6	2.3±0.5	11.4
Eu	0.074±0.015	0.085	0.50	0.39	0.72±0.06	9.7
Gd	0.32±0.07	0.36	2.1	1.1	3.1±0.7	9.7
Tb	0.049±0.010	0.054	0.32	0.22	0.57±0.11	11.6
Dy	0.31±0.07	0.33	1.94	1.17	3.8±0.7	12.3
Ho	0.073±0.014	0.077	0.45	0.22	0.80±0.16	11.0
Er	0.21±0.04	0.22	1.29	0.95	2.3±0.6	11.0
Tm	0.033±0.007	0.033	0.19	0.16	0.38±0.09	11.5
Yb	0.17±0.03	0.17	(1.00)	(1.00)	2.0±0.4	11.8
Lu	0.031±0.005	0.031	0.18	0.09	0.35±0.09	11.3
Y	1.8±0.3	3.5	21	30	22±5	12.2
Sc	8.3±1.4	32	190	---	35±6	4.2

<sup>a</sup>Data for chondrites were taken from Tables 1, 2, and 3. (±) values are mean deviations.<sup>b</sup>Average weighted Si in these 20 meteorites is 16.0%, taken from average Si abundances in these categories as given by MASON (1962-3), CRAIG (1964), UREY and CRAIG (1953), and MASON and WIHK (1964).<sup>c</sup>Normalized to Yb at 1.00 from previous column.<sup>d</sup>Normalized values of Yb at 1.00 by CLAYTON and FOWLER (1961) and CLAYTON, FOWLER, HULL, and ZIMMERMAN (1961).<sup>e</sup>Achondrites were Juvinas, Nuevo Laredo, Pasamonte, and Stannern.<sup>f</sup>Ratios of values in column 6 to values in column 2.<sup>g</sup>Values of Allegan, Richardson, Holbrook, and Modoc are excluded. If the high Ce values of Holbrook and Modoc are included, the average Ce value is raised to 0.95.

CHONDRITES

Absolute concentrations of the individual REE in 20 chondritic meteorites range from  $0.15 \pm 0.01$  ppm La in an enstatitic chondrite (Abee) to  $0.46 \pm 0.01$  ppm La in a Type III carbonaceous chondrite (Mokoia) (see Tables 1 and 2). On the other hand, normalized abundance distributions relative to Yb at unity indicate negligible (<15 per cent) internal fractionation of the REE and Sc among the five principal kinds of chondritic meteorites and even among the three types of carbonaceous chondrites. Since the over-all absolute abundance of any of the REE or Sc in a given chondrite may be known to better than  $\pm 10$  per cent, some apparent differences in the normalized abundances may reflect the over-all uncertainty of the abundance values. For example, in Type I carbonaceous chondrites, the average normalized La value in two chondrites (column 2 of Table 5) is  $\sim 16$  per cent less than the average normalized La value in 20 chondrites (column 9 of Table 5). If real, an  $\sim 16$  per cent fractionation is still trivial compared with differences in the internal fractionation of terrestrial matter (discussed below).

In any case, the lack of significant internal RE and Sc fractionation within the five chondritic categories and the average mean deviation of  $\sim \pm 20$  per cent in absolute RE and Sc abundances (e. g., La =  $0.30 \pm 0.06$  ppm, Table 8) of all 20 chondrites strongly reinforce the earlier observations by UREY and CRAIG (1953) that the compositions of chondritic meteorites are fairly uniform. In Figs. 1 and 3, the average RE abundances, with associated mean deviations, in 20 chondrites and in four Ca-rich eucritic achondrites have been plotted, respectively.

Atomic ratios of  $\text{La}/10^6 \text{Si}$ ,  $\text{Yb}/10^6 \text{Si}$ , and  $\text{Sc}/10^6 \text{Si}$  listed in Table 7 indicate that the REE and Sc have decreased steadily in concentration relative to Si in the order carbonaceous, ordinary, Sokobanitic, and enstatitic chondrites. (The lack of appreciable internal RE fractionation (i. e., relative to each other) in all chondritic categories

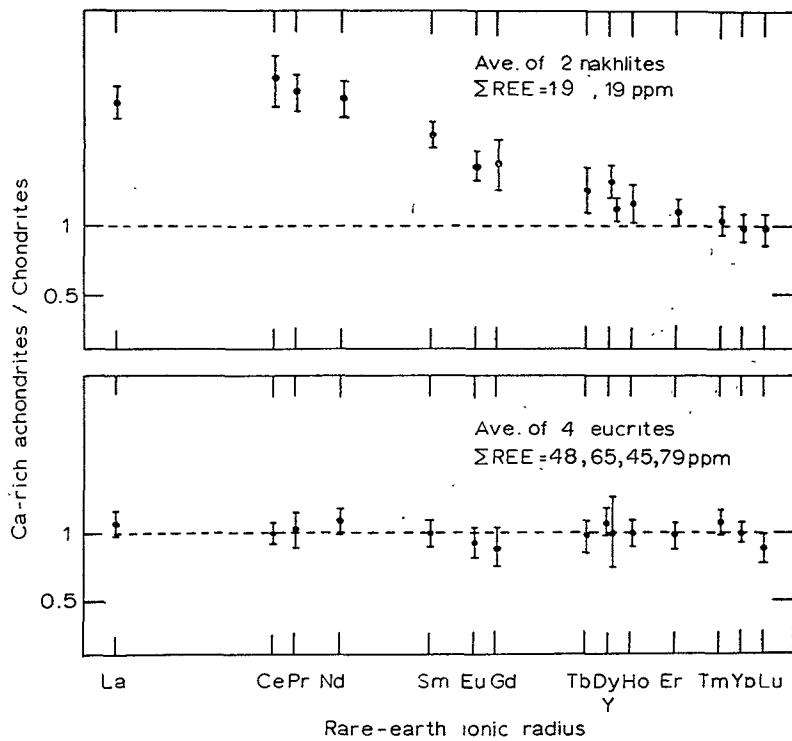


Fig. 3. Comparison plot for four Ca-rich achondrites (Table 3).

(Table 5) allows the convenient use of Yb as well as La as a representative REE.) In Table 7, the ( $\pm$ ) values are the mean deviations of the respective ratios. There appears to be no significant difference between the atomic ratios in H- and L-group chondrites, but a difference of a factor of two exists between the atomic ratios in enstatitic and carbonaceous chondrites. Within the carbonaceous chondrite family, fractionation relative to Si may have occurred to some degree for La but to a negligible degree for Yb and the other REE. It was pointed out above that La may have been internally fractionated to  $\sim$ 16 per cent with respect to the other 13 REE in Type I carbonaceous chondrites. Assuming  $\sim$ 16 per cent internal fractionation, the corrected  $\text{La}/10^6 \text{Si}$  ratio is  $0.36/0.84 = 0.43$   $\text{La}/10^6 \text{Si}$  atoms in Type I carbonaceous chondrites. Therefore, the  $\text{La}/10^6 \text{Si}$  ratios in Types I, II, and III are 0.43, 0.47, and 0.51, respectively, which may indicate some degree of REE fractionation--up to  $\sim$ 15 per cent--with respect to Si. The element Y, not a lanthanide, also shows no fractionation relative to Si among the carbonaceous chondritic subgroups and decreases in concentration similarly to the lanthanides for the other chondritic groups.

Since no definite priority can be assigned to the various chondritic classes with regard to their primitiveness, the atomic abundances of the REE and Sc must range within a factor of 2. UREY (1964) has recently summarized the status of chondrites as follows: "Though the composition of the chondrites is remarkably constant as compared with terrestrial rocks, important variations in the concentrations of certain major and minor constituents occur which make it impossible to conclude that any one type of chondrite could have been produced from another by simple physical processes.. This is true for the carbonaceous, enstatitic, and high- and low-iron-group chondrites."

In some recent oxygen isotopic studies of minerals in chondritic meteorites and terrestrial rocks by REUTER, EPSTEIN, and TAYLOR (1965) and TAYLOR, et al. (1965), the  $\text{O}^{18}/\text{O}^{16}$  ratio (on a per mil basis relative to mean standard ocean water) showed a regular decrease from

Type I through Type III carbonaceous chondrites, i. e., ~12 per mil for one Type I, 10 ±1 per mil for two Type II; and from ~ -1 to 6 per mil for three Type III, as compared with a rather narrow range of 4.6 to 6.2 per mil for 28 whole-rock chondrites. The oxygen isotopic data from these studies do not suggest which of the three carbonaceous classes might be most "primordial," since differentiation or metamorphism of any carbonaceous-like matter toward ordinary chondritic matter could also induce oxygen isotopic fractionations. The oxygen isotopic data seem to indicate that oxygen fractionation within the carbonaceous classes is inversely related to a possible over-all RE fractionation (Table 7).

Very similar  $O^{18}/O^{16}$  ratios were reported for pyroxenes separated from ordinary chondrites, enstatitic chondrites and achondrites, and nakhlites. These different meteoritic classes are thus very probably genetically related. The lack of internal RE and Sc fractionation in these ordinary and enstatitic chondritic classes is consistent with the idea of similar physicochemical histories during some stages of their formation, while the severe internal RE and Sc fractionation observed in enstatitic achondrites and nakhlites (see below for further details) suggests very different histories in explanation of their over-all mineralogy.

In Table 7, the atomic ratios obtained by RNAA overlap within the mean deviation with those found by INAA (parenthetical values). Up to 25 per cent Sc fractionation with respect to Si may have occurred within the carbonaceous chondrite family, and, in general, Sc has been fractionated with respect to Si in the five main chondritic groups to the same degree as the REE. The average Sc ratios obtained from INAA, based on many more analyzed meteorites, indicate less Sc fractionation relative to Si among the chondritic groups than do the data from RNAA. In any case, Sc, relative to Si, is definitely lower in abundance in enstatitic chondrites, from 1.5 to 2.2, than in Type II carbonaceous chondrites. To summarize, the small number of analyzed meteorites in each group does not permit a definite conclusion about differences in degree of fractionation between the REE and Sc.

In general, the abundances of the majority of the nonvolatile chemical elements in carbonaceous or ordinary chondrites agree, after appropriate normalization, with solar elemental abundances (with the exception of iron) (see ALLER, 1961, 1965). This observation strongly suggests that chondritic meteorites are the best available specimens for the study of original nebular abundances. At present, no concurrence exists among students of meteorites, as to which of the five chondritic categories best represents primitive matter, i. e., matter closely identical in abundances to the nebula from which the solar system evolved--see ANDERS (1964) and UREY (1964) for extensive discussions on this point.

Table 9\* contains, for convenient reference, the average atomic abundances of the macroconcentrated elements Na, Mg, Al, Ca, Cr, Mn, Fe, Co, and Ni ( $>10^3$  atoms/ $10^6$  Si atoms) and the trace elements Sc and Cu in the various chondritic classes. These data, taken from various sources, seem to represent in the opinion of the authors (SCHMITT, GOLES, and SMITH, 1966) the most reliable experimental values for macro-quantity and trace elements in all the chondritic classes. In most of the meteoritic literature to date, abundances have been established for other elements for quite a number of meteorites in only a few meteoritic classes or for only a few meteorites over all the meteoritic classes.

Many of the elemental abundances (Na, Sc, Cr, Mn, Co, and Cu) in Table 9 were determined via INAA, while others were obtained by well established analytical methods. Note that fractionation among the chondritic classes seems most pronounced for Na and Mn; these two elements are the most accurately determined (to  $\pm 3$  per cent) via INAA in meteorites. Fractionation has been demonstrated for the other elements to varying degrees. The striking similarity of the abundances in Type III-B and L-group chondrites strongly suggests that Type III-B chondrites may be the best precursors for the latter. (SCHMITT and SMITH, 1964c). Unfortunately, no RE or Sc abundance data exist for the Type III-B chondrites.

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\* See SCHMITT, GOLES, and SMITH (1966) for a slight revision of this table.

Table 9. Average Atomic Abundances in Chondrites Relative to  $10^6$  Si Atoms

Chondrite Type	Meteorite	Na ( $\times 10^3$ )	Mg ( $\times 10^4$ )	Al ( $\times 10^3$ )	Ca ( $\times 10^3$ )	Sc	Cr ( $\times 10^2$ )	Mn ( $\times 10^2$ )	Fe ( $\times 10^4$ )	Co ( $\times 10^2$ )	Ni ( $\times 10^3$ )	Cu ( $\times 10$ )
I Carbonaceous	Alais Ivuna Orgueil	62±2 (3)	103±6 (3)	100±15 (3)	69±9 (3)	36±8 (3)	117±11 (3)	92±3 (3)	85±5 (3)	23±1 (3)	45±5 (3)	72±30. (3)
II Carbonaceous	Al Rais Boriskino Cold Bokkeveld Mighei Murray Renazzo Santa Cruz	33±5 (6)	104±3 (11)	91±6 (11)	73±11 (11)	35±4 (7)	122±13 (7)	65±4 (7)	87±4 (7)	20±2 (7)	45±2 (11)	40±5 (7)
III-A	Felix Groznaia Kaba Lance Mokoia Vigarano	29±3 (5)	107±2 (6)	106±15 (6)	81±6 (6)	41±10 (6)	118±4 (6)	51±5 (6)	80±3 (6)	19±1 (6)	42±2 (6)	33±3 (5)
	Karoonda Ornans Warrenton	28±3 (3)	107±3 (3)	87±8 (3)	66±3 (3)	38±5 (3)	117±4 (3)	50±4 (3)	81±3 (3)	20±1 (3)	42±2 (3)	36±4 (3)
III-B	Chainpur Ngawi Tieschitz	43±1 (3)	84±8 (2)	66±10 (2)	41±1 (2)	29±4 (3)	98±3 (3)	67±4 (3)	58±9 (2)	14±3 (3)	29±5 (2)	21±1 (3)
Ordinary H-Group		45±3 (20)	96±2 (27)	78±16 (27)	53±7 (27)	31±4 (20)	121±10 (20)	73±5 (20)	81±3 (27)	24±3 (20)	44±5 (27)	26±3 (20)
		46 (M1)	86 (M1)	74 (M1)	52 (M1)		92 (M1)	78 (M1)	82 (M1)	25 (M1)	46 (M1)	
Ordinary L-Group		45±4 (29)	93±2 (30)	68±14 (30)	51±5 (30)	29±3 (29)	106±9 (29)	74±6 (29)	59±2 (30)	14±3 (29)	29±4 (30)	26±8 (29)
		46 (M1)	94 (M1)	71 (M1)	51 (M1)		90 (M1)	74 (M1)	58 (M1)	15 (M1)	28 (M1)	
Ordinary SB-Group		43±3 (10)	94±3 (12)	76±2 (12)	47±7 (12)	26±1 (10)	106±9 (10)	71±4 (10)	50±3 (10)	12±3 (10)	23±5 (12)	28±6 (10)
Enstatites		48±9 (4)	80±11 (9)	55±16 (9)	24±8 (9)	26±6 (4)	92±6 (4)	80±14 (4)	75±11 (9)	23±2. (4)	44±6 (9)	36±4 (4)
		46 (M2)	79 (M2)	61 (M2)	35 (M2)		79 (M2)	53 (M2)	76 (M2)	26 (M2)	41 (M2)	

NOTE: (±) values indicate mean deviations. Numbers in parentheses indicate number of meteorites analyzed.

This table was taken from SCHMITT, SMITH, and GOLES (1965), and SCHMITT and SMITH (1965).

Recently, RINGWOOD (1965) and GREENLAND and LOVERING (1965) have reiterated their point of view that Type I carbonaceous chondrites represent the nearest approach to the original cosmic proportion of the elements, based principally on the observed fact that this particular group has the highest trace elemental abundances. If ordinary chondritic meteorites are the result of metamorphic processes acting on carbonaceous-like (Type I) matter, then no appreciable internal fractionation and over-all differentiation occurred for the REE and Sc in these two categories (see Table 7).

In view of the above discussion, no particular RE and Sc atomic ratios relative to the standard element Si for any of the five chondritic groups have a definite priority. Since abundances of many chalcophilic elements in carbonaceous and in many enstatitic chondrites agree fairly well with solar abundances and these elements are generally depleted by up to many orders of magnitude in ordinary chondrites, and since concentrations of the rare noble gases are higher in carbonaceous and enstatitic chondrites than in ordinary and Soko-Banjitic chondrites, abundance patterns of the nonvolatile chemical elements in carbonaceous and enstatitic chondrites are generally accorded more significance. From Table 7, a definite difference of a factor of roughly two exists between atomic ratios of the REE and Sc in carbonaceous and enstatitic chondrites.

The RE and Sc abundances have been established (Table 2) in Abee, Indarch, and St. Marks; the first two are classed as Type I enstatitic chondrites and St. Marks is classed as a Type II enstatitic chondrite by ANDERS (1964). Type I enstatitic chondrites contain an abundance of the "deficient" elements (i. e., those that are scarce in ordinary chondrites), although they show a slight depletion in these elements relative to Type I carbonaceous chondrites. ANDERS (1964) has suggested that the carbonaceous chondrites accreted from two types of matter, an undepleted fraction-A that separated from its nebular gases at low temperature (now associated with the matrix minerals) and a fraction-B, or high

temperature component, that separated from the gases at high temperature (now identified with the chondrules plus metal). In terms of Ander's model, the Type I enstatitic chondrites consist predominately of fraction-A matter. Comparison of the RE and Sc abundances in Tables 1 and 2 indicates that in terms of absolute abundances, the abundances in Type I carbonaceous and Type I enstatitic chondrites are very similar and, therefore, not inconsistent with Ander's model. But since the RE and Sc abundances in St. Marks are only  $\sim 40$  per cent higher than the corresponding averages in Abee and Indarch, not too much weight should be attached to this correlation.

The pronounced affinity of Y and the lanthanides for phosphates would account for their residence in the phosphate minerals. GREENLAND and LOVERING (1965) have recently obtained P abundances of  $1260 \pm 120$  ppm for eight H-group ordinary chondrites and  $1110 \pm 150$  ppm for 31 L-group ordinary chondrites ( $\pm$  values being standard deviations) and MASON (1965b) reports 1100 and 1200 ppm P for the H- and L-group chondrites, respectively. There thus seems to be no statistical difference in the P contents of the two ordinary chondritic classes. P is a predominantly lithophilic element in stony meteorites, occurring mainly in apatite (MASON, 1962) and whitlockite (FUCHS, 1962) minerals. Assuming that the REE reside in these phosphate minerals, the near similarities of the RE abundances within their rather large dispersions (Table 7) and the overlap of phosphate mineral contents in these two chondritic classes indicate that the RE concentrations in the phosphate minerals for ordinary chondritic classes are approximately equal.

On the other hand, a direct correlation of RE abundances and P does not extend to enstatitic chondrites, where an inverse correlation seems to exist. Both MASON (1965a) and GREENLAND and LOVERING (1965) observed a distinct enrichment of P in enstatitic chondrites relative to ordinary chondrites. Perhaps an appreciable fraction of P may be present as the iron-nickel phosphide (schreibersite) which precludes any

speculations regarding the REE-phosphate distributions in enstatitic chondrites.

MASON (1965b) reports 122, 90, and 76 P atoms relative to  $10^4$  Si atoms in Types I, II, and III carbonaceous chondrites, respectively. This trend seems to be inversely correlated with RE fractionation among the carbonaceous groups. Owing to the large RE dispersions among these groups, no unequivocal conclusions concerning REE-P correlations may presently be drawn for the carbonaceous chondrites. Analyses for the REE and Sc in the various meteoritic minerals and chondrules must be performed in order to establish their residency. Since the concentrations of K (assumed normatively in feldspar) in enstatitic and Type I carbonaceous chondrites are nearly the same and the anorthite component of plagioclase feldspars may contain few lanthanides (SCHIEBOLD, 1931), it seems unlikely that the decreased RE abundance in enstatitic chondrites relative to Type I carbonaceous chondrites is associated with a decrease in plagioclase mineral. However, this conclusion is based on the assumption of the same RE content in the plagioclase minerals (of a common sink) for these two chondritic classes, which may not necessarily be the case.

It has been suggested (MASON, 1962; RINGWOOD, 1961; ANDERS, 1964; WOOD, 1963) that carbonaceous chondrites represent the closest approach to primitive matter and that the ordinary, Soko-Banjitic, and enstatitic chondrites resulted from metamorphic or physicochemical processes acting on carbonaceous chondritic matter. For self-consistency with such processes and no appreciable movement of Si, the REE and Sc have been appreciably fractionated by a factor of  $\sim 2$  with respect to Si in the formation of the enstatites and fractionated by  $\sim 20$  per cent with respect to Si in the formation of ordinary chondrites. With respect to the formation of ordinary chondrites by metamorphic processes from Type II or III carbonaceous chondritic matter, it seems curious that  $\sim 20$  per cent diffusion (Table 7) of the REE and Sc out of a system undergoing metamorphism would leave them apparently unfractionated with respect to each other. On the other hand, if Type I carbonaceous chondritic-like matter

was the precursor of ordinary chondrites, less (say <10 per cent) diffusion of the lanthanides and Sc occurred, but some fractionation (say ~5 per cent) of Y may have occurred.

In summary, it may be concluded that the normalized data of Tables 5 and 7 clearly indicate that no appreciable internal fractionation of the REE and Sc occurred during the physicochemical processes that were responsible for their fractionation with respect to Si in the formation of the various classes of chondritic meteorites.

The fractionation of other trace elements with respect to Si shows some definite trends, as was pointed out by ANDERS (1964). In Table 10, some very recent atomic abundances of ten trace elements in five main chondritic categories have been compiled. For almost all elements, the abundances of two or more meteorites in each class were determined, which gives some significance to the tabulated average values. The atomic abundances of almost all the trace elements--with their large differences in chemical properties, such as lithophilic (Zn, Zr), siderophilic (Cu, Ga, Pd), and chalcophilic (Se, Zn, Cu, Cd, Te, Ag, Pd)--are about twice as great in Type I carbonaceous chondrites as in Types II and III carbonaceous chondrites. For most trace elements given in Table 10, fractionation differences between Types II and III have been much less than between these types and Type I. This trend is reversed for the trace REE and Sc (Table 7), with a possible depletion of 10 to 20 per cent occurring for Type I relative to Types II and III, and essentially no appreciable fractionation differences exist between Types II and III. Even upon comparison of the REE and Sc with the lithophilic trace elements Zr and Zn, an opposite fractionation pattern seems present among the carbonaceous classes. Fragmentary data, i.e., abundances for only one or two meteorites in each carbonaceous class, for Sr (MURTHY and COMPSTON, 1965), Ba (REED, KIGOSHI, and TURKEVICH, 1960), and U (REED, KIGOSHI, and TURKEVICH, 1960, and GOLES and ANDERS, 1962), of all these heavy lithophilic trace elements approximate the RE and Sc trends among the carbonaceous groups.

Table 10. Some Recent Atomic Abundances, Relative to  $10^6$  Si Atoms,  
of Ten Trace Elements in Various Kinds of Chondritic Meteorites

Element	Carbonaceous			Ordinary	Enstatitic	
	Type I	Type II	Type III		Type I	Type II
Cu <sup>a</sup>	840	500	470	260	570	370
Zn <sup>b</sup>	2100	600	450	130	890	42
Ga <sup>c</sup>	51	31	23	12	35	35
Se <sup>d</sup>	89	32	21	13	48	32
Zr <sup>e</sup>	32	23	20	16	24	---
Pd <sup>d</sup>	4.2	2.2	2.7	1.6	2.6	2.3
Ag <sup>d</sup>	1.0	0.3	0.4	0.12	0.7	0.2
Cd <sup>f</sup>	2.3	1.0	0.5	0.07	3.5	0.1
Te <sup>d</sup>	2.0	3.8	1.1	1.0	4.2	0.6

<sup>a</sup>Average of data by GREENLAND and GOLES (1965) and SCHMITT, GOLES, and SMITH (1966).

<sup>b</sup>GREENLAND and GOLES (1965).

<sup>c</sup>GREENLAND (1965b).

<sup>d</sup>GREENLAND (1965a).

<sup>e</sup>SCHMITT, BINGHAM, and CHODOS (1964).

<sup>f</sup>Average values taken from SCHMITT, SMITH, and OLEHY (1963) and GREENLAND (1965a).

As part of their abundance determinations of some 16 elements in chondrites, GREENLAND and LOVERING (1965) measured the lithophilic trace elements Sr, Ba, and Sc in one Type I and four Type III carbonaceous and six enstatitic chondrites. They report values of 23 (Type I) and 43 (Type III) for Sr; 19 (Type I) and 18 (Type II) for Ba; and 38 (Type I) and 42 (Type III) for Sc in carbonaceous chondrites (all in atoms/ $10^6$  Si atoms). They point out that these Ba values could reflect a systematic error due to incorrect standard normalization. However, their Sc values agree with those in Table 7, while the Sr data suggest some possible fractionation within the carbonaceous groups, which is consistent with the RE data. Sr, Ba, and Sc atomic abundances of 35, 13, and 27, respectively, were determined by Greenland and Lovering in enstatitic chondrites. Although statistics are poor, the Sr and Ba data suggest less depletion in abundances for enstatitic versus carbonaceous chondrites than the RE depletion in these two chondritic classes.

The paucity of abundance data on Sr, Ba, and U by other workers for enstatitic chondrites does not permit any clear comparison of these elements with the REE and Sc in such chondrites. Where present, abundances of Sr, Ba, and U do suggest a depletion in enstatitic chondrites relative to carbonaceous chondrites, which is generally consistent with the trend for REE and Sc. For example, Ba atomic abundances were  $3.9 \pm 0.3$  and  $2.2 \pm 0.1$  in five ordinary chondrites and two Type I enstatitic chondrites, respectively (REED, KIGOSHI, and TURKEVICH, 1960). These abundances are definitely in line with the RE and Sc values given in Table 7 for corresponding chondritic classes.

No significant difference in atomic abundances of Sr, Ba, and Sc for H- and L-group chondrites ("falls") was detected by GREENLAND and LOVERING (1965). The absence of RE fractionation within these two groups has been noted in Table 7.

All the trace elements, including the lithophilic elements Zr and Zn, in Table 10 show appreciable depletions, from 2 to  $10^3$ , in ordinary

chondrites relative to Type I carbonaceous chondrites. Over-all fractionation of the REE and Sc for these two meteoritic classes is no more than 10 per cent. Within their dispersions, similar 10 per cent differences have been reported for Sr, Ba, and U.

The nearly similar fractionation patterns among the various chondritic classes exhibited by the lithophilic trace elements, REE, Sc, Sr, Ba, and U may conceivably be associated with the commonly large ionic radii, varying from 0.80 to 1.34 Å, and large coordination numbers, ranging from 6 to 12, of these elements. Substitution in the predominant and accessory meteoritic minerals may be controlled to a considerable degree by the ionic radii and coordination number of the trace elements. (See, for example, GOLDSCHMIT, 1954, and RANKAMA and SAHAMÁ, 1950, for extended discussions on trace element substitution.) Mechanisms for trace element fractionation will be adequately tested only after the following experimental studies have been carried out:

1. Abundance determination of additional selected, relatively non-volatile, lithophilic trace elements (e.g., Sr, Zr, Ba, Th, U, Hf, Nb, Ta) in at least five meteorites from each meteoritic class.
2. Establishment of partition coefficients as a function of temperature of some of the above trace elements in a variety of principal and accessory meteoritic minerals.
3. Determination of trace element diffusion coefficients in a wide spectrum of silicate systems.

Since a large body of atomic abundance data already exists for many chalcophilic and siderophilic elements, as listed in Table 10, experiments similar to (2) and (3) above would be immensely helpful in understanding their abundance relationships and those of the chondritic groups per se. To supplement experiment (3), troilite and metallic systems should be investigated as well as the silicate systems.

Normalized abundances of 2.8 and 2.5 have been obtained for Ce in two H-group chondrites, Allegan and Richardton,\* respectively, and appear to be low by a factor of  $\sim 2$  relative to the average normalized value of  $5.0 \pm 0.4$  (Table 5). These values have therefore been deleted from the normalized values of Table 5 and from the average Ce value. In general, the normalized Ce values, relative to Yb at 1.00, vary from 4.1 to 9.8. Ce values for Holbrook and Modoc, two L-group ordinary chondrites, are 9.2 and 10.0, respectively, considerably higher (by a factor of  $\sim 2$ ) than the average normalized Ce value of  $5.0 \pm 0.4$  (Table 5). No explanation for the anomalously high Ce contents in Holbrook and Modoc is obvious.

It has been noted by ZAOZERSKII and PATKIN (1959) that Ce may easily be oxidized to the tetravalent state by atmospheric oxygen under conditions of increased pH and temperature. If the REE are introduced into the crystallizing minerals of the chondritic matrix with resultant enhancement of the Ce abundance due to oxidation of some or all of the Ce to the tetravalent state, it is conceivable that the abundances of other tetravalent ions such as Ti, Zr, Hf, and Th may be increased. Since the ionic radii of  $Zr^{+4}$ ,  $Hf^{+4}$ , and  $Th^{+4}$  at  $0.79$ ,  $0.78$ , and  $1.02$  Å, respectively (AHRENS, 1952), are within 20 per cent of the ionic radius of  $Ce^{+4}$  at  $0.94$  Å, some admission of  $Zr^{+4}$ ,  $Hf^{+4}$ , and  $Th^{+4}$  with  $Ce^{+4}$  would be expected in a geochemical distribution of trace elements in silicate minerals and rocks (GOLDSCHMIDT, 1954). No difference was observed between the Zr abundance in Modoc--Ce was a factor of about 2 greater in Modoc and Holbrook than other normalized Ce values in the L-group chondrites (see Table 5)--and Zr abundances in seven other L-group chondrites (SCHMITT, BINGHAM, and CHODOS, 1964). The absence of electronegativity data for  $Ce^{+4}$  precludes comparison with the electronegativity criterion (see AHRENS, 1964b) for discussion of other criteria

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\* These two meteorites were the first two studied by SCHMITT, et al. (1960).

in his article entitled "Chemical Bond and Geochemical Distribution of Elements"). However, from a compilation of electronegativities (AHRENS, 1964a) and comparison of electronegativities for elements with multiple oxidation states, the Ce<sup>+4</sup> electronegativity value should be quite similar to Zr<sup>+4</sup> and Hf<sup>+4</sup>. No reliable abundance data for Hf in the chondrites Holbrook or Modoc exist.

MOORE and BROWN (1962), in their analysis of Ti via spectrographic techniques, found no significant difference in the concentration of Ti in both Modoc and Holbrook relative to 18 other L-group chondrites. Since the ionic radius of Ti<sup>+4</sup> is 0.68 Å, no appreciable admission of Ti<sup>+4</sup> would be expected.

In their neutron activation analysis of Th in stone meteorites, BATE, HUIZENGA, and POTRATZ (1959) found Th abundances in Modoc and Holbrook to be essentially similar to those in three other chondritic meteorites.

In summary, the lack of increased Zr and Th substitution and the presence of Ce substitution in these two meteorites almost forces the conclusion that properties other than ionic charge and radius, e.g., complex ion formation and stabilities, may be responsible for their unique Ce enrichment. A study of RE and Sc abundances in separated chondritic minerals may help clarify this problem.

In a recent publication, SCHMITT, SMITH, and OLEHY (1964) discussed the apparently large Ce/La ratio in Orgueil, a Type I carbonaceous chondrite, which is particularly interesting because of the possible existence of fossilized organisms in Orgueil (see a discussion by Urey, et al., in "Life Forms in Meteorites," 1962). From their normalization of the RE and Sc data to La at unity, they concluded that Ce and Yb were apparently enhanced in Orgueil relative to normalized abundances in 17 chondrites. Upon normalization of Yb to unity (column 2 of Table 5), it has been observed that only La may have been fractionated in Orgueil and Ivuna, relative to 20 chondrites. In conclusion, their discussion of an

enhanced Ce abundance does not seem justified by an inspection of the normalized abundances of Table 5.

The absolute abundances in chondritic meteorites of Eu and Sc determined by BATE, POTRATZ, and HUIZENGA (1960) and of Sc determined by KEMP and SMALES (1960), in both cases via neutron activation analysis, agree well with those reported in Tables 1 and 2. Such close agreement again underscores the homogeneity of chondritic meteorites and the accuracy of the activation technique.

If the elemental atomic abundances (Table 8, column 3) of the odd-Z and even-Z REE are plotted (SCHMITT, et al., 1963) versus RE atomic number, the odd-Z abundances define a smoothly decreasing function from La to Lu with a perturbation, or bump, at the element Ho. For even-Z elements, the Ce peak is pronounced and a peak also occurs between Gd and Tb. On the average, the odd-Z RE abundances are about four times less than the average of the elemental abundances of the two adjacent even-Z REE. This alternating, or saw-tooth, behavior of elemental abundances with the even-Z elements in greater abundance was pointed out by HARKINS (1917). To a first approximation, the higher even-Z RE abundances may be attributed to the greater number of stable isotopes for the even-Z REE. With the single exception of Eu, the odd-Z elements are essentially monoisotopic with respect to the s- and r-processes in nucleosynthesis (the stable isotopes in low abundance, e.g., La<sup>138</sup> and Lu<sup>176</sup>, are produced via the p-process (CLAYTON and FOWLER, 1961)). Since there are effectively four stable isotopes per even-Z element, a smooth nucleosynthetic production over the mass-number range from 139 to 175 will result in a roughly quadruple increase in even-Z elements over the odd-Z elements.

From the average absolute and relative RE abundances in 20 chondrites given in Table 8, the total isobaric abundances of even-A and odd-A elements were calculated (see Fig. 4). Abundance of Ba, preceding the REE, is taken from REED, KIGOSHI, and TURKEVICH (1960), and

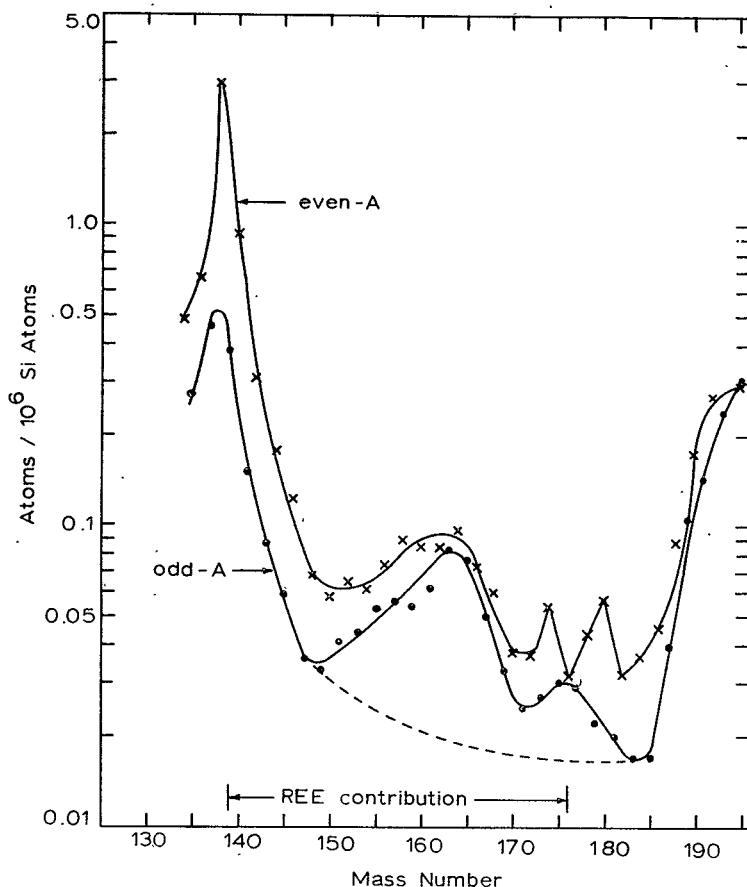


Fig. 4. Average abundances (in atoms per  $10^6$  Si atoms) of REE in 20 chondrites for both even- $A$  and odd- $A$  mass numbers; average errors in abundances are  $\sim \pm 10$  per cent. For  $A \leq 138$ , a Ba abundance of 4.1 and an interpolated abundance for Xe of 3.8 were used; for  $A \geq 176$ , the following abundances were used: Hf, 0.16; Ta, 0.020; W, 0.12; Re, 0.046; Os, 0.66; Ir, 0.38; and Pt, 0.92 (all in atoms per  $10^6$  Si atoms--see UREY, 1964).

abundances of elements after mass 175 from the collected data of UREY (1964). The abundance of Xe was interpolated at 3.8 atoms/ $10^6$  Si atoms. A smooth decrease is found in both odd-A and even-A abundances from  $A \approx 138$  to  $A \approx 150$ . A smooth perturbation in the gradual decline in abundances is noted between  $A \approx 150$  and  $A \approx 170$ , with peaks appearing at  $A \approx 163$ . This has been explained by BECKER and FOWLER (1959) from considerations of the rapid neutron-capture process in supernovae and the spheroidal nuclear deformations in the REE region. CAMERON (1959) attributes the peaks at  $A \approx 163$  to the fission (on a fast time scale) of very heavy nuclei with a 184-neutron closed shell. Another interpretation by CAMERON (1962) involves the absorption of limited numbers of neutrons by closed shell nuclei, which results in the formation of broad peaks near  $A \approx 163$ .

The first major REE contribution occurs for even-A abundances at  $A = 140$  via  $\text{Ce}^{140}$  and for odd-A abundances at  $A = 139$  via  $\text{La}^{139}$ . For the odd-A curve, the  $\text{La}^{139}$  contribution helps delineate clearly the peak at  $A \approx 138$ ; which is attributable to the magic 82-neutron shell on the slow time scale. For the even-A curve, the  $\text{Ce}^{140}$  abundance defines a symmetrical peak at  $A \approx 138$ . For an extensive discussion of this peak due to the effect of the magic nuclear shell, the reader is referred to AHRENS (1964a).

For the odd-A mass distribution pattern beyond  $A = 170$ , another smooth peak appears at  $A \approx 175$ . This peak has been largely defined by activation analysis of the following elements in chondritic meteorites: Yb and Lu, by SCHMITT, et al. (1963a), and SCHMITT, SMITH, and OLEHY (1964); Hf, by SETZER and EHMANN (1964); Ta, by ATKINS and SMALES (1960) and EHMANN (1962); W, by AMIRUDDIN and EHMANN (1962) and ATKINS and SMALES (1960); Re and Os, by Hirt, Geiss, and Houtermans (see UREY, 1964) and BATE and HUIZENGA (1963); Ir, by RUSHBROOK and EHMANN (1962) and NICHIPORUK and BROWN (1962); and Pt, by NICHIPORUK and BROWN (1962), HAMAGUCHI, NAKAI, and ENDO (1961).

HAMAGUCHI, NAKAI, and KAMENTO (1961), and HAMAGUCHI, NAKAI, and IDENO (1961). The odd-A mass values are based on the following abundances from  $A = 171$  through 195:  $\text{Yb}^{171}$ ,  $\text{Yb}^{173}$ ,  $\text{Lu}^{175}$ ,  $\text{Hf}^{177}$ ,  $\text{Hf}^{179}$ ,  $\text{Ta}^{181}$ ,  $\text{W}^{183}$ ,  $\text{Re}^{185}$ ,  $\text{Re}^{187}$  ( $\sim 25$  per cent and  $\text{Os}^{187}$   $\sim 75$  per cent),  $\text{Os}^{189}$ ,  $\text{Ir}^{191}$ ,  $\text{Ir}^{193}$ , and  $\text{Pt}^{195}$ . Continuing the rapidly decreasing solid curve from  $A = 139$  to  $A = 147$  and then following the dashed curve through  $A = 183$ , it becomes obvious that the peak at  $A \sim 163$  is about four times and the peak at  $A \sim 175$  about two times above the "dashed baseline." Beyond  $A \sim 185$ , the odd-A distribution curve rises smoothly and abruptly, reaching another peak at  $0.31 \text{ atom}/10^6 \text{ Si atoms}$  for  $A = 195$  ( $\text{Pt}^{195}$ ).

For the even-A mass distribution pattern beyond  $A = 170$ , two peaks exist at  $A = 174$  and  $A = 180$ , with a steep rise occurring from mass 182 to another peak at  $A = 194$ . The peak at  $A = 174$  is real, since it is defined by  $\text{Yb}$  isotopes,  $\text{Yb}^{172}$  and  $\text{Yb}^{174}$ , whose isotopic fractions are 0.218 and 0.318, respectively. Abundances of  $\text{Hf}^{178}$ ,  $\text{Hf}^{180}$ , and  $\text{W}^{182}$  largely define the peak at  $A = 180$ . Any valid theory of nucleosynthesis must obviously account not only for the major features of the general abundance distribution but also for minor peaks, whether broad or narrow.

Following the general approach of BURBIDGE, et al. (1957), CLAYTON, et al. (1961), CLAYTON and FOWLER (1961), and, more recently, SEEGER, FOWLER, and CLAYTON (1964), have quantitatively studied the problem of nucleosynthesis of the heavy elements from the viewpoint of neutron capture in stellar interiors on slow ( $10^2$ - $10^4$  yr) (s-process) and fast (seconds) (r-process) time scales. Assuming that the RE distribution pattern in chondrites represents the abundance distribution in the primitive solar nebula, the REE provide a long, continuous range over atomic numbers ( $Z = 57$ -71) and mass numbers ( $A = 139$ -176) for one of the best tests of nucleosynthetic theories. In the mass range from 150 to 180, the major contribution for synthesis seems to be the r-process. For the odd-A masses, the s-process accounts for  $\sim 10$  per cent

of the observed abundances; consequently the *r*-process, responsible for ~90 per cent, has a large peak within the RE range at  $A = 163$ , with a smaller synthesis peak at  $A = 175$ . The *s*-process contributes to production of a larger fraction,  $\gtrsim 20$  per cent, of the even-*A* species, with a significant peak in the *r*-process occurring at  $A = 164$  and satellite peaks at  $A = 174$  and  $A = 180$ . Within the framework of the above theory, accurate calculations of theoretical abundances demand more neutron capture cross-section measurements in the tens of kilovolt range; see MACKLIN and GIBBONS (1965) for a discussion on this point.

Using the physics of deformed nuclei in the RE mass region, SEEGER, FOWLER, and CLAYTON (1964), have found--to a first approximation--a broad peak near  $A \sim 163$  in their theoretical calculations. In view of the approximations required to make feasible a computer calculation of the *r*-process abundances, it is certainly an important first step that they succeeded in quantitatively reproducing a broad peak at  $A \sim 163$  in addition to the sharp peaks at  $A \sim 138$  and 195. Further refinements of such complicated functions as the mass equation, lifetime predictions of beta decay, and deformation parameters for highly enriched neutron nuclei in this region will perhaps delineate and reproduce the two peaks in this highly sensitive RE portion of the "cosmic" abundance distribution curve.

It has been suggested by WOOD (1963) on the basis of mineralogic and petrographic evidence that chondrules (small stony spheroids  $\sim 1$  mm in diameter scattered throughout the chondritic matrix) predate the chondritic meteorites and that chondrules condensed out of the primitive solar nebular matter. Presumably, unmetamorphosed chondrules from carbonaceous chondrites might represent best the primitive solar system matter. To test this hypothesis, SCHMITT, SMITH, and GOLES (1965), used the technique of INAA to measure the abundances of Na, Sc, Cr, Mn, Fe, Co, and Cu in more than 250 chondrules. Average abundances of these seven elements in the chondrules agreed better with solar abundances (ALLER, 1961) than the corresponding abundances in chondritic meteorites.

Another severe test of the Wood hypothesis rests on the abundance pattern of the REE and Sc in a wide variety of chondrules.\*

The presently available RE abundance data for 20 chondritic meteorites and the absence of serious internal fractionation of the REE (despite differences in over-all RE differentiation by a factor of 2 with respect to Si over the five chondritic classes) strongly suggest that the present RE distribution pattern in chondrites represents that of the original nebular matter from which our solar system was formed. That the theoretical RE abundances agree fairly satisfactorily with the experimental RE abundances in chondrites lends support to the RE distribution pattern observed in chondritic meteorites.

For the majority of meteorites (see Tables 1, 2, 3, and 4), the elemental abundances were determined (SCHMITT, et al., 1963, and SCHMITT, SMITH, and OLEHY, 1964) via two isotopes of several elements: Ce via  $\text{Ce}^{141}$  and  $\text{Ce}^{143}$ ; Gd via  $\text{Gd}^{159}$  and  $\text{Tb}^{161}$ ; Er via  $\text{Er}^{169}$  and  $\text{Er}^{171}$ ; Yb via  $\text{Yb}^{169}$  and  $\text{Yb}^{175}$ ; and Lu via  $\text{Lu}^{176}$  and  $\text{Lu}^{177}$ . In other words, the isotopic ratios of the five elements Ce, Gd, Er, Yb, and Lu were determined and these agreed within the 95 per cent confidence level with corresponding ratios for terrestrial matter. (For the element Eu, the two isomers of mass 152 resulted from neutron capture of the single stable nuclide  $\text{Eu}^{151}$ .) Such excellent agreement indicates that the REE in meteoritic matter originated from the same source as did the REE in terrestrial matter. Especially sensitive to any nucleosynthetic model is the isotopic ratio of  $\text{Yb}^{168}/\text{Yb}^{174}$ .  $\text{Yb}^{168}$  is produced via the p-process (successive proton capture or  $(\gamma, n)$  processes) and  $\text{Yb}^{174}$  by the r-process (0.29) and by the s-process (0.71) (CLAYTON, et al., 1961). The other elements (Lu excepted) with the specified isotopic ratios result from both the s-process and the r-process.

The isotopic ratio of  $\text{Yb}^{168}/\text{Yb}^{174}$  is also important from another standpoint. Since the thermal-neutron-capture cross sections of  $\text{Yb}^{168}$  and  $\text{Yb}^{174}$  are 11,000 and 60 barns, respectively, the isotopic ratios of

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\* SCHMITT, SMITH, and OLEHY (1965) have observed significant internal RE fractionation in chondrules from the ordinary chondrites Allegan and Richardson and less internal fractionation in chondrules from the carbonaceous chondrites Chainpur and Mokoia.

these two isotopes could be drastically different in meteoritic and in terrestrial material with respect to their original abundances if the primitive solar nebula (REE included) was subjected to different degrees of thermal neutron irradiation or to different mixing conditions after neutron irradiation (FOWLER, GREENSTEIN, and HOYLE, 1962).

More sensitive ( $\pm 0.5$  per cent) RE isotopic ratios of Sm<sup>149</sup> ( $\sigma = 40,800$ )/Sm<sup>154</sup> ( $\sigma = 5.5$ ), Eu<sup>151</sup> ( $\sigma = 3200$ )/Eu<sup>153</sup> ( $\sigma = 440$ ), and Gd<sup>157</sup> ( $\sigma = 242,000$ )/Gd<sup>158</sup> ( $\sigma = 3.9$ ) have been obtained by MURTHY and SCHMITT (1963) through a combination of neutron activation and mass spectrometric techniques.\* Within experimental error ( $\pm 0.5$  per cent), the terrestrial and meteoritic isotopic ratios are identical for these sensitive isotopic pairs. From this agreement, one may infer that both meteoritic and earth materials were well mixed after the presumed solar bombardments. A more detailed discussion and alternative explanations are given in the work of Murthy and Schmitt.

The abundance of one REE, Yb, has been determined in the sun by ALLER (1962). He initially found an abundance ratio of 1.1 Yb atoms/ $10^6$  Si atoms in the solar atmosphere (ALLER, 1961), and subsequently (ALLER, 1962) used the new f-values of CORLISS and BOZMAN (1962) to obtain a value of 5.9 Yb atoms/ $10^6$  Si atoms. These values are based on a single Yb resonance line ( $\lambda 3988$ ) and the Yb value has been given dubious assessment. These solar Yb/Si ratios are 6 and 31 times (respectively) greater than the ratio (0.17 Yb atoms/ $10^6$  Si atoms, Table 8) in 20 chondritic meteorites. Ratios of Ba atoms/ $10^6$  Si atoms (Ba immediately precedes the REE La) in the solar atmosphere, based on eight Ba lines, and in chondritic meteorites of 3.9 (ALLER, 1961) and 4.0 (REED, *et al.*, 1960), respectively, have been found.

WALLERSTEIN (1965a,b) has recently measured the abundances of Y and the Ce group (La-Gd) relative to Sc in the sun and also in six F-stars

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\* In these ratios, the values in parentheses are the cross sections in barns for thermal neutron capture.

from curves of growth of ionized lines (Table 11). Six F-stars were studied because they have a considerable range of over-all metal content. In Table 11, Wallerstein's data have been renormalized to the Sc meteoritic value of 32. Additionally, the abundances in the sun and in the six F-stars of Sr, Zr, and Ba relative to Sc at 32 agree fairly well with meteoritic values. Relative to Sc, abundances of the elements Y, Ce, Sm, and Gd agree within a factor of 2 with meteoritic values, while La and Nd abundances in both the sun and six F-stars seem too high by factors of 3 to 7 relative to corresponding meteoritic values. Because of the possibly incorrect line identification for Pr and the weak Eu and Gd lines, not too much reliance must be placed on their abundance values.

The general similarity of RE and other elemental abundances (e.g., Sr, Zr, and Ba) relative to Sc indicates no significant difference in metallic constituency between these metal-rich and metal-poor stars. La, with its many prominent lines for certainty of identification, seems to be significantly more abundant in all these stars than in meteorites. Further work on f-values for the REE may help to clarify this La discrepancy.

It becomes immediately obvious from the general similarity of the abundances of the heavy elements in the sun, six F-stars, and chondritic meteorites that quite similar nuclear reactions must have been responsible for the synthesis of these metals in the sun and six F-stars. Further solar-abundance studies of the REE will allow a comparison of the relative RE abundances in the outer third portion of the sun and in chondrites, and will show if the REE have been fractionated in the sun in the absence of chemical processes. The hypothesis by UREY (1952) that chondritic meteorites represent the best available "primordial" matter of our solar system has been tested and found acceptable on the basis of abundance similarities in chondritic meteorites and in the sun.

Abundances of ratios of Y to Si in the solar atmosphere have been found to be  $5.7 \text{ Y}/10^6 \text{ Si atoms}$  by ALLER (1961) and  $50 \text{ Y}/10^6 \text{ Si atoms}$  by

Table 11. Comparison of Atomic Abundances of REE  
and Sc in the Sun, 6 F-Stars, and 20 Chondritic  
Meteorites  
(Relative to  $10^6$  Si Atoms)

Element	Sun <sup>a</sup>	Mean of 6 F-stars <sup>b</sup>	20 Chondritic Meteorites <sup>c</sup>
Sc	(32)	(32)	32
Y	6.4	3.2	3.5
La	2.6	1.3	0.38
Ce	1.3	1.3	1.05
Pr	(0.8)	---	0.15
Nd	2.1	(2.1)	0.71
Sm	0.6	0.5	0.24
Eu	(0.3)	---	0.085
Gd	(0.3)	---	0.36

<sup>a</sup> Values of WALLERSTEIN (1965a) renormalized at Sc to 32.

<sup>b</sup> Values of WALLERSTEIN (1965b) renormalized at Sc to 32.

<sup>c</sup> Taken from column 3 of Table 8.

ALLER (1962) based on new f-values of CORLISS and BOZMAN (1962). The solar values are 1.6 and 14 times (respectively) greater than the ratio  $3.5 \text{ Y atoms}/10^6 \text{ Si atoms}$  (Table 8) in chondritic meteorites. Solar atmospheric values of  $20 \text{ Sc atoms}/10^6 \text{ Si atoms}$  were obtained by ALLER (1961, 1962). New f-values for Sc have changed the Sc/Si ratio only by 1 per cent. The Sc/Si ratio in the sun is 0.7 times the ratio in chondritic meteorites.

#### Ca-RICH ACHONDRITES (EUCRITES)

Absolute abundances of the REE and Sc have been established (SCHMITT, et al., 1963, and SCHMITT, SMITH, and OLEHY, 1964) in four Ca-rich eucritic (or basaltic) achondrites (see Table 3, columns 3-6). In general, the average abundances (Table 8, column 6) of the REE in these achondrites are about 11.5 times greater than the corresponding average abundances in 20 chondrites.

Upon normalization of the RE data to  $\text{Yb} = 1.00$  (Table 6, column 2), it is observed that no appreciable RE fractionation has occurred in these four Ca-rich achondrites relative to chondrites (see Table 5, column 9, and Fig. 3). This absence of fractionation is a rather surprising observation, because it has been hypothesized (FISH, GOLES, and ANDERS, 1960) that achondritic matter has been subjected to rather extensive reworking and recycling at high temperatures. Since the structures of achondrites are similar to those of terrestrial rocks, where melting processes have been important (UREY and CRAIG, 1953), and in which the REE have been severely fractionated, internal fractionation of the REE in these achondrites was expected.

The average Sc abundance of  $35 \pm 6$  ppm in four eucrites (Table 8) compares well with the average Sc value of  $28 \pm 4$  ppm (SCHMITT and SMITH, 1964a, and SCHMITT, GOLES, and SMITH, 1966) determined via INAA in smaller mass specimens from eight eucrites and two howardites; the four eucrites of Table 3 were included in this INAA study. From the Sc value in Table 8, it is noted that this element has been enriched  $\sim 4.2$  times in

the four eucritic achondrites with respect to chondrites, while the RE and Y concentrations in these four Ca-rich achondrites have been increased about 11.5 times. This strong fractionation, plus the fact that concentrations of the lithophilic REE, Zr, Be, Th, and U (see references above) are increased by 7 to 10 times in these Ca-rich eucritic achondrites, restricts these achondrites to nearly the same physicochemical histories. The small mean deviations of the major constituents (UREY and CRAIG, 1953; DUKE, 1963) and of the average abundances of Na, Sc, Cr, Mn, Fe, Co, and Cu (SCHMITT and SMITH, 1964a, and SCHMITT, GOLES, and SMITH, 1966) in these Ca-rich eucritic achondrites and the recent petrographic study by DUKE (1963) substantiate the hypothesis of similar histories of formation. Since some Ca minerals carry the REE and the ionic radius of Ca at 0.99 Å favors isomorphous substitution of REE (with ionic radii varying from 1.14 to 0.85 Å), an enrichment of Ca in these achondrites may be partially or wholly responsible for the RE enhancement.

In a compilation of chemical analyses of basaltic achondrites (the four Ca-rich eucritic achondrites of Table 8 were included) by A. D. Maynes (see DUKE, 1963) and UREY and CRAIG (1953), DUKE (1963) has calculated an apatite content of ~0.2 per cent on a normative basis. If the partition coefficients for the REE in terrestrial basaltic minerals are valid (see below), then, to a first approximation, this relatively large concentration of apatite may well be the primary residence mineral for the REE in those Ca-rich eucritic achondrites.

UREY and CRAIG (1953) have drawn attention to the similarity between eucrites and howardites (Ca-rich achondrites) and terrestrial oceanites and olivine basalts. Both types of matter presumably underwent melting and differentiation processes. Since the REE in these achondrites have not fractionated, whereas the REE in terrestrial sediments, volcanic basalts, etc., are generally fractionated in favor of the light REE (see the later discussion on terrestrial matter), the melting and differentiation processes may have been considerably different in the meteorite parent bodies and on the earth.

In the Ca-rich basaltic-type achondrites, and in a mésosiderite, no anomalous abundances of the two REE Ce and Eu have been observed relative to the abundances in all five classes of chondrites. Both of these elements have oxidation states ( $\text{Ce}^{+3}$ ,  $\text{Ce}^{+4}$  and  $\text{Eu}^{+2}$ ,  $\text{Eu}^{+3}$ ) other than trivalent which may be indicators of the redox environment of the meteorite or its parent. Obviously, redox conditions may change and relative RE abundance ratios (e.g., La/Ce and La/Eu) can remain unaltered if mass transport did not take place. In the presence of atmospheric  $\text{O}_2$  and at a raised temperature, Ce may be oxidized to tetravalent Ce, whose chemical properties become similar to the fourth group, e.g., to Th and Ti. Therefore, the transformation from some "primary" matter to eucritic matter apparently occurred under O-poor conditions. Also, redox conditions were unfavorable for reduction of  $\text{Eu}^{+3} \rightarrow \text{Eu}^{+2}$ . The REE Sm and Yb also have +2 oxidation states which may be reached if large reduction potentials (in standard states) of -1.72 v for  $\text{Sm}^{+3} \rightarrow \text{Sm}^{+2}$  (VICKERY, 1961) and -1.15 v for  $\text{Yb}^{+3} \rightarrow \text{Yb}^{+2}$  (Vickery, cited by ROSSINI, *et al.*, 1952) are available. Chemical conditions unfavorable to  $\text{Eu}^{+3}$  reduction will obviously be unpropitious for  $\text{Sm}^{+3}$  and  $\text{Yb}^{+3}$  reduction. It has been shown recently by CORYELL and CHASE (1961) that  $\text{Fe}^{+2}$  may reduce  $\text{Eu}^{+3}$  if the  $(\text{OH}^-)^2/(\text{SO}_4^=)$  ratio is less than  $10^{-11.3}$ . For example, the  $\text{Eu}^{+2} \rightarrow \text{Eu}^{+3}$  reaction at standard states is 0.43 v, while in the presence of sulfate the voltage reduces to -0.04 v. Divalent  $\text{Eu}^{+2}$  would presumably undergo diadochic substitution in  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ , or  $\text{Ba}^{+2}$  minerals, thereby showing anomalous abundances.

The similarity of the relative RE distribution patterns in chondrites and Ca-rich eucritic achondrites assumes prime importance in any discussion of the primordiality of solar system matter, since it has been found (FREY and HASKIN, 1964) that nearly identical absolute (within a factor of 2) and relative RE abundance distribution patterns exist in three basalts from the mid-Atlantic ridge and in one from the experimental Mohole compared with chondrites and these Ca-rich achondrites. (These

data are discussed in detail in the section on terrestrial REE.) Hence, any chemical and petrological similarities between these Ca-rich eucritic achondrites and chondrites may clarify genetic relationships between the stony meteoritic families and may suggest mechanisms for fractionation of terrestrial matter.

It has been suggested by MOORE (1962) and MASON (1962) in mineralogical and petrological studies that Ca-rich eucritic and howarditic achondrites may be derived by differentiation of chondritic matter. Eucritic and howarditic achondrites, also known as pyroxene-plagioclase achondrites (MASON, 1962), are quite similar in composition. The mineral constituency of the eucrites consists principally of pigeonite and plagioclase, and that of the howardites of hypersthene and plagioclase. Minor quantities of hypersthene and pigeonite are present in the eucrites and howardites, respectively. Since both achondritic groups resemble terrestrial basalts closely in over-all composition and somewhat in structure, it seems logical at first glance to assume a direct genetic relationship to chondritic matter. Enrichment of Ca and Al by a factor of ~5 and the REE, Zr, Ba, Th, and U by factors of 7 to 12 in these Ca-rich achondrites seems consistent with a magmatic differentiation mechanism.

VINOGRADOV (1958) has pointed out that alkali elements tend to concentrate in terrestrial silica-rich rocks. However, UREY and CRAIG (1953) and EDWARDS (1955) found that the alkalis Na and K were depleted in Ca-rich achondrites by a factor of ~2 relative to chondrites, which is opposite to the expected trend since Ca-rich achondrites contain ~47 to 53 per cent  $\text{SiO}_2$  as compared with ~38 per cent  $\text{SiO}_2$  in ordinary chondrites and ~33 per cent  $\text{SiO}_2$  in Type II carbonaceous chondrites. Na abundances of  $3050 \pm 440$  ppm recently obtained in accurate INAA by SCHMITT and SMITH (1964a) and SCHMITT, GOLES, and SMITH (1966) have corroborated the work of EDWARDS (1955). Since alkali halides may be volatilized from silicate melts, UREY (1957) and GAST (1960) suggested

that the alkali elements were lost from the Ca-rich achondrites via a volatilization mechanism. Any appreciable volatilization via alkali halide loss, say via NaCl, may be ruled out on the basis of cosmic abundance arguments. Recently, a Cl abundance of  $2200 \text{ Cl atoms}/10^6 \text{ Si atoms}$  in Type I carbonaceous chondrites has been determined by GREENLAND (1963), while SUESS and UREY (1956) have adopted a maximum value of  $8850 \text{ Cl atoms}/10^6 \text{ Si atoms}$  in order to retain reasonable odd and even mass curves. Since the Na abundances (SCHMITT, GOLES, and SMITH, 1966) in Types I, II, and III carbonaceous chondrites are  $(62 \pm 2) \times 10^3$ ,  $(33 \pm 5) \times 10^3$ , and  $(29 \pm 3) \times 10^3 \text{ Na atoms}/10^6 \text{ Si atoms}$ , respectively, the total "cosmic" Cl concentrate could have volatilized only  $\sim 0.2$  of the Na present in the assumed chondritic precursors of these Ca-rich achondrites. On the other hand, ALLER (1961) gives an astronomical value of  $3 \times 10^5 \text{ C atoms}/10^6 \text{ Si atoms}$ , and such a Cl concentration would be sufficient for volatilization of Na and other alkali elements. But since the abundances of major and minor elements (including chalcophilic elements) in the carbonaceous chondrites agree well with solar values, the measured Cl abundance in Type I carbonaceous chondrites should approximate the solar system value.

Mass spectrometric analyses by NORMAN, et al. (1964), of Cs vaporized from a silicate base at  $800^\circ\text{C}$  in a vacuum indicate that the preponderance ( $>99$  per cent) of the Cs leaves the melt as atomic Cs. A small fraction may leave as CsO. Similar volatility behavior as single atoms may be expected for the other alkali elements.

From Table 12, which contains the ratios of alkali elemental abundances in chondrites and corresponding ratios in Ca-rich achondrites, a similarity is observed for the Na/K ratios (7.6 and 7.8) and Rb/Cs ratios (from 11 to 340 and 21) in these two types of meteorite matter. The Rb/Cs ratio of  $28 \pm 7$  obtained by GAST (1960) nearly overlaps the median value of 37 found by SMALES, et al. (1964), in 22 ordinary chondritic meteorites (falls). However, since the Rb/Cs ratios ranged from 11 to 340 in the

Table 12. Comparison of Ratios of Alkali Elemental Abundances in Chondrites and in Ca-rich Achondrites (Eucrites and Howardites)<sup>a</sup>

	Na/K	Rb/Cs	K/Rb	K/Cs
Ordinary chondrites	7.6±1.2	28±7 (37 <sup>b</sup> ) (12, 13, 20 <sup>c</sup> )	280±50	7,500±1,700
Ca-rich achondrites	7.8±2.3	21±5	1,360±320	29,000±8,000

<sup>a</sup>Na values in more than 50 ordinary chondrites and in ten Ca-rich achondrites are from SCHMITT and SMITH (1963c, 1964a) and SCHMITT, GOLES, and SMITH (1966); K values in ~34 ordinary chondrites are from EDWARDS (1955) and KIRSTEN, KRANKOWSKY, and ZÄHRINGER (1963), and K values in seven Ca-rich achondrites are from KIRSTEN, KRANKOWSKY, and ZÄHRINGER (1963); Rb and Cs values (determined in same meteorites) in five ordinary chondrites and four Ca-rich achondrites are from GAST (1960). (±) values are mean deviations.

<sup>b</sup>Rb and Cs data from SMALES, et al. (1964), determined in 22 ordinary chondritic meteorites ("falls") yield a median value of 37 over a range from 11 to 340 and an average value of 84 ±72.

<sup>c</sup>Ratios in Types I, II, and III carbonaceous chondrites from SMALES, et al. (1964).

22 chondrites, ambiguous correlations between the Rb/Cs ratios in chondrites and Ca-rich achondrites will necessarily follow. For single meteorites in Types I, II, and III carbonaceous chondrites, SMALES, et al. (1964), reported Rb/Cs ratios of 12, 13, and 30, respectively. Assuming that Types I and II carbonaceous chondrites represent the closest approach to primordial abundances, the 13 and  $21 \pm 5$  values for the Rb/Cs ratios in carbonaceous chondrites and Ca-rich achondrites, respectively, suggest a depletion of Cs of  $\sim 50$  per cent relative to Rb in Ca-rich achondrites.

In absolute amounts, Rb and Cs have been depleted in Ca-rich achondrites  $\sim 10$  times relative to ordinary chondrites (GAST, 1960). And, as noted above, the pair Na and K have been correspondingly depleted by  $\sim 2$  times. These depletion factors suggest a similar mechanism for Na and K removal and another mechanism for Rb/Cs removal. These mechanisms could be identical for all alkalies but enhanced  $\sim 5$  times for Rb and Cs.

Diffusion coefficient data on the alkalies in silicates are somewhat meager, and those available were obtained at scattered temperatures. RALKOVA (1962) measured the diffusion of Li, Na, K, and Cs in a silicate mixture of  $620^{\circ}\text{K}$  and found a linear relationship from Li through Cs in a plot of  $\log D$  versus the reciprocal of the ionic radius. In particular, values of  $\log D$  ( $\text{cm}^2/\text{sec}$ ) of Na, K, and Cs at  $-9.6$ ,  $-11.5$ , and  $-12.4$ , respectively, reveal a much slower (by  $\sim 10^3$ ) diffusion of Cs than Na.

Recently, NORMAN and WINCHELL (1965) performed diffusion studies on the alkali elements--using radionuclides--in a  $1450^{\circ}\text{K}$  eutectic  $\text{CaO-Al}_2\text{O}_3-\text{SiO}_2$ . Diffusion coefficients,  $D$ , may be expressed conveniently as  $\log D = A - (B/T)$ . Relationships between the constants A and B and the reciprocal ionic radii were found to correlate linearly; i. e., A and B both increased uniformly with increasing ionic radius or its decreasing reciprocal. Specific  $\log D$  ( $\text{cm}^2\text{-sec}^{-1}$ ) values obtained in the above eutectic experiment at  $1450^{\circ}\text{K}$  for Na, K, Rb, and Cs were  $-6.7$ ,  $-8.0$ ,

-8.4, and -8.6, respectively. At  $1000^{\circ}\text{K}$ ,  $\log D$  values are extrapolated to -9.8, -13.3, -14.1, and -15.0 for Na, K, Rb, and Cs, respectively. Therefore, at  $1450^{\circ}\text{K}$ ,  $\sim 20$  times more Na than K will diffuse out of a similar siliceous matrix. Alkali diffusion coefficients for the particular eutectic matrix mentioned above approach each other ( $\log D \sim -4.8$ ) at  $\sim 2000^{\circ}\text{K}$ . In order for a constant Na/K ratio to have been preserved and also for both Na and K to have been depleted by a factor of  $\sim 2$  in an assumed magmatic differentiation of chondritic-like matter to Ca-rich achondrites as one of the primary products, temperatures of  $\sim 2000^{\circ}\text{K}$  must have been attained. If the magmatic temperature was  $< 2000^{\circ}\text{K}$  and the relative order of diffusivities for the alkali elements was retained in a molten chondritic magma as observed for the calcia-alumina-silica eutectic, surficial heating (UREY, 1957) of large objects will not deplete Cs relative to Na since the loss of the heavy alkalies will be more diffusion-limited. Experimental data on diffusion coefficients of the alkalies in chondritic silicate melts at  $> 2000^{\circ}\text{K}$  are badly needed to test the differentiation processes alluded to above.

In summary, similarity of the Na/K ratios in chondritic and Ca-rich achondritic matter suggests a magmatic temperature of  $\sim 2000^{\circ}\text{K}$ . For temperatures lower than  $2000^{\circ}\text{K}$ , strong fractionation of the alkali elements would have occurred in the above meteoritic genetic relationship, which is contrary to observation, at least for Na and K. The wide variability of the Rb/Cs ratio within the chondritic family, per se, may be associated with temperatures higher than  $2000^{\circ}\text{K}$  in a semi-closed system (gas escape allowed) at which the  $D(\text{Cs})$  may be greater than  $D(\text{Rb})$ .

A temperature of  $2000^{\circ}\text{K}$  is near the melting point,  $1940^{\circ}\text{K}$ , of a typical calcium phosphate, whitlockite, which presumably may carry the RE phosphates. At such a high temperature, appreciable diffusion and subsequent fractionation of the REE could have occurred. Conversely, magmatic fractionation could have consisted principally of gravitational segregation of high melting minerals such as olivines, which have

presumably low REE and other heavy element contents. Such a model would provide for convenient enrichment of the REE with negligible, say <10 per cent, internal fractionation of the REE (DUKE, 1965).

Also, ANDERS (1964) has noted that since the abundances of volatile elements like Hg and Cd (EHMANN and HUIZENGA, 1959; REED, KIGOSHI, and TURKEVICH, 1960; SCHMITT, SMITH, and OLEHY, 1963) appear undepleted in these Ca-rich achondrites relative to ordinary chondrites, loss of alkalies during magmatic differentiation seems quite unlikely. However, if the Ca-rich achondrites resulted from magmatic differentiation of carbonaceous chondrites, this observation by Anders does not apply, since Hg and Cd and other elements are depleted by more than an order of magnitude in Ca-rich achondrites relative to carbonaceous chondrites.

On an atomic abundance basis relative to Si, abundances of Na, K, and Rb are comparable in Type II carbonaceous and ordinary chondrites but Cs has been depleted by ~3.5 in ordinary chondrites relative to Type II carbonaceous chondrites. Assuming Type II carbonaceous chondritic-like matter to be the precursor involved in differentiation to Ca-rich achondrites, the initial Rb/Cs weight ratio of ~13 in these carbonaceous chondrites would compare to ~21 in Ca-rich achondrites (see UREY, 1964, and Table 12), indicating a loss of Cs relative to Rb in the magmatic process.

SMALES, et al. (1964), have recently conducted some volatility experiments on chondritic meteorites in order to measure the relative loss of the alkalies K, Rb, and Cs. Their preliminary results suggest that the alkali elements can indeed be fractionated out of ordinary and carbonaceous chondrites at high temperature, ~1300° to 1500°K. For example, an average loss of ~90 per cent Rb was associated with a loss of ~95 per cent Cs, which is certainly in accordance with the data of Table 12. These data would tend to support the hypothesis of high temperature magmatic differentiation of carbonaceous chondritic matter to Ca-rich achondrites with an associated loss by a factor of ~2 of the alkali elements Na and K, loss by a factor of ~10 of Rb and Cs, and increase of the Rb/Cs ratio from 13 to 21.

Recently, some  $O^{18}/O^{16}$  isotopic data by TAYLOR, et al. (1964), REUTER, EPSTEIN, and TAYLOR, (1965), and TAYLOR, et al. (1965), have placed serious restrictions on hypothesis with respect to derivations of basaltic achondrites from chondrites. These investigators found that the  $O^{18}/O^{16}$  ratios in meteoritic pyroxenes divide stony meteorites into five groups: (1) carbonaceous chondrites ( $\sim 0.5/\text{mil}$ ); (2) basaltic, mesosideritic, and hypersthene achondrites ( $\sim 3.8$  to  $4.4/\text{mil}$ ); (3) nakhlites ( $5.3$  to  $5.5/\text{mil}$ ); (4) enstatitic, H-group, and L-group chondrites, and enstatitic achondrites ( $5.4$  to  $6.3/\text{mil}$ ); and (5) ureilite ( $8.6/\text{mil}$ ).

Similarities were found in the  $O^{18}/O^{16}$  ratios of plagioclase minerals in the basaltic and hypersthene achondrites and in silicate portions of mesosiderites, thereby indicating a close relationship between these materials. Furthermore, on the basis of whole rock  $O^{18}/O^{16}$  analyses, the  $\delta(O^{18}/O^{16})$  per mil values ranged from  $4.3$  to  $4.6$  and  $4.8$  to  $6.0$  for basaltic achondrites and ordinary chondrites, respectively. The differences in the O isotopic ratios cited for pyroxenes correlate well with the observed ratios found in the whole rock.

In an assumed magmatic differentiation of ordinary chondritic matter to Ca-rich achondrites, the  $O^{18}/O^{16}$  ratios in pyroxenes were decreased by  $\sim 2$  per mil in the Ca-rich achondrites relative to ordinary chondrites. On the other hand, an increase of 1 to 2 per mil was observed for terrestrial basaltic rocks relative to ultramafic rocks. The latter were presumably precursors of the former in differentiation. The inverse changes in the O isotopic ratio preclude any direct comparison of terrestrial and meteoritic fractionation. If Ca-rich achondrites represent a differentiation product of chondritic-like matter, the Ca-rich, or basaltic, achondrites must have been exposed to a different O reservoir than were the terrestrial basalts and gabbros. The overlap observed by the above workers in  $O^{18}/O^{16}$  analyses for whole rock chondrites and terrestrial ultramafic rocks strengthens the concept that the above two "primitive" rock systems are related, perhaps by some simple mechanism.

In summary, the similarities in the Na/K ratios for chondrites and Ca-rich achondrites suggest a genetic relationship, while the terrestrial analogy of magmatic differentiation does not support such a relationship. Perhaps the near anhydrous conditions during the magmatic differentiation of ordinary chondrites to Ca-rich achondrites in contrast to terrestrial ultramafic to basalt fractionation may be responsible for the observed inverse  $O^{18}/O^{16}$  ratio changes.

A wide range, -0.8 to 12.2 per mil, was measured in six whole rock carbonaceous chondrites by TAYLOR, et al. (1965), as compared to a narrow range, 4.3 to 4.6 per mil, for basaltic achondrites. Three Type III carbonaceous chondrites (Mokoia, Felix, and Vigarano) have O values of -0.8, 3.0, and 5.5 per mil, which are below and close to the corresponding basaltic achondritic values. Strict comparison of increasing  $O^{18}/O^{16}$  ratios for terrestrial fractionation of basalts from ultramafic rock (see above) suggests that Type III carbonaceous chondrites may have been precursors of the basaltic achondrites.

From an extensive study of composition and other properties of basaltic and mesosideritic achondrites, DUKE (1963) suggests the derivation of basaltic achondrites from a magmatic differentiation of parental matter high in calcium plagioclase, in contrast to the sodic-plagioclase chondritic constituency. Moreover, according to Duke, the parental matter of an Estherville-like mesosiderite could have been the starting composition. Supporting evidence for this hypothesis is found in recent results of DUKE (1965) which show concentrations of Na, K, Rb, Cs, Sr, Ba, U, Ca, Sc, Mn, Ti in mesosiderites and basaltic achondrites to have more or less regular variations as a function of the (Fe/Fe + Mg) ratios. However, in view of the non-internal-fractionation of the REE in the Ca-rich achondrites as compared with chondrites and a slight internal RE fractionation (~20 per cent in the mesosiderites, as discussed below), the direct genetic relationship between the mesosideritic and basaltic achondrites seems untenable, unless the over-all fractionation process of mesosideritic

silicates to basaltic achondrites just reverses the 20 per cent internal RE fractionation observed in mesosideritic silicate. This phenomenon seems highly improbable.

Since the REE, Zr, Ba, Th, and U are enriched up to ten times in Ca-rich achondrites relative to chondrites, about ten volumes of chondritic matter must have been magmatically differentiated for these trace elements during the formation of one volume of Ca-rich achondrites (SCHMITT and SMITH, 1964a). Assuming that the observed meteoritic fall ratio is proportional to the actual volume ratio for stone meteorites and that Ca-rich achondrites are derived from chondritic matter, the observed ratio of meteoritic falls for Ca-rich achondrites to ordinary chondrites agrees within a factor of 2 with the predicted enrichment of trace elements in Ca-rich achondrites.

No data exist on the partition and concentration of the REE, Sc, Zr, Ba, Th, U, and many other trace elements among the minerals of either chondritic or achondritic meteorites. Only with this sort of experimental information can hypothesis on fractionation at high temperatures of trace elements before or after accretion of precursory chondritic matter be checked and compared with RE distribution patterns in minerals of terrestrial rock (CHASE, et al., 1963; TOWELL, WINCHESTER, and SPIRN, 1965; BALASHOV, 1963b).

The Ca-rich eucritic abundances of the REE and Sc show (Table 8, last column) that Y was fractionated in these achondrites to the same degree, within experimental error, as were the lanthanides relative to chondrites. The major accessory minerals for REE residence probably are the chloroapatites and other phosphate compounds. Such is not the case for Sc, which fractionated ~4.2 times in the Ca-rich achondrites relative to chondrites. Even though the  $\text{Sc}^{+3}$  radius of  $0.81 \text{ \AA}$  is close to the  $0.85 \text{ \AA}$  radius of the last REE,  $\text{Lu}^{+3}$  (AHRENS, 1952), and, therefore, has some chemical properties similar to those of the REE, GOLDSCHMIDT (1954) has pointed out that the geochemistry of  $\text{Sc}^{+3}$  probably is governed

to a large extent by diadothic replacement in ferromagnesian minerals in view of the similarity in ionic radii of Sc<sup>+3</sup>, 0.81 Å; Mg<sup>+2</sup>, 0.66 Å, and Fe<sup>+2</sup>, 0.74 Å.

Electronegativity values of Sc (1.20) and Mg (1.23), another measure of chemical behavior, may favor Sc substitution in Mg minerals but are different from the heavy REE (1.11) and considerably less than Fe<sup>+2</sup> (1.64). Perhaps the ionic difference between Sc<sup>+3</sup> (0.81 Å) and Lu<sup>+3</sup> (0.85 Å), which are similar, and Ca<sup>+2</sup> (0.99 Å) is sufficient to favor more Lu<sup>+3</sup> and other RE<sup>+3</sup> substitution than Sc<sup>+3</sup> in Ca minerals (e.g., chlorapatite or merrillite).

Recently, Sc abundances have been determined by INAA (SCHMITT, GOLES, and SMITH, 1966) in separated pyroxene minerals of Ochansk (an L-group chondrite); 11 ppm and 29 ppm Sc were observed in two pyroxene fractions, the higher value being obtained in a pyroxene fraction that probably had some plagioclase (inferred from x-ray diffraction lines). About 8 ppm Sc was also found in an olivine mineral separate. Since ~60 per cent by mass of the average H-group chondrites are pyroxene and olivine minerals in Ochansk (~20 per cent metallic iron), ~20 per cent of the remaining mass may be attributed to minerals such as plagioclase, oligoclase, and troilite, and to secondary minerals such as chromite, apatite (~0.4 per cent), etc. WAGER, SMITH, and IRVING (1958) also reported Sc enriched in pyroxene separated from ferrogabbro. BALASHOV (1963b) and STEUBER and GOLES (1964) have noted the accumulation of Sc in ultrabasic and basic rocks, probably by isomorphic replacement of Mg<sup>+2</sup> and Fe<sup>+2</sup> in olivines and pyroxenes. Such data, admittedly fragmentary, strongly suggest that Sc concentrates in ferromagnesium minerals, with a small fraction in apatite, where the REE and Y undoubtedly reside.

From recent REE data (TOWELL, WINCHESTER, and SPIRN (1965) for terrestrial gabbros and granites, the partition coefficients of REE in apatite and other minerals such as plagioclase feldspars, hornblende, augite, biotites average  $\sim 10^4$  for the light REE La and  $10^2$  to  $10^4$  for the

heavy REE Yb. These coefficients are expressed in reference to apatite, e. g., (ppm La in apatite)/(per cent apatite in rock)/(ppm La in feldspar)/(per cent feldspar in rock). If Sc were largely confined to pyroxene and olivine and the REE to phosphate minerals in chondrites, fractionation of a chondritic-like melt would be expected to reveal differences in the degree of Sc and REE fractionation in the Ca-rich achondrites, one of the fractionation products. Also, the presumed (AHRENS, 1964a, b) absence of ligand field effects for  $\text{Sc}^{+3}$  compared with the well-known complex formation of  $\text{REE}^{+3}$  and  $\text{Y}^{+3}$  could effect differences in magmatic processes.

#### MESOSIDERITES

Absolute abundances of the REE and Sc determined (SCHMITT, et al., 1963, and SCHMITT, SMITH, and OLEHY, 1964) in the silicate phases of two observed "falls" of mesosiderites, Estherville and Veramin, are about three times greater than and approximately equal to, respectively, the RE contents in ordinary chondrites (Table 3, columns 7 and 8). In these two falls, the lanthanides and Y have been uniformly fractionated relative to chondrites (Fig. 5), e. g., La normalized to Yb at unity, to 1.2 in Estherville and to ~0.8 in Veramin. Fractionation of Sc tends to follow the same trend exhibited by the slopes for the REE. However, Sc has been enriched ~40 per cent and depleted ~20 per cent in Veramin and Estherville, respectively, relative to the extrapolated REE slopes. SCHMITT, et al. (1963), reported no significant fractionation in Estherville in their first interpretation of the data. Also, the element Eu has been enriched ~1.4 times, relative to the expected uniform Eu fractionation with adjacent REE.

Mesosiderites, which are composed of approximately equal amounts of silicates and nickel iron, are closely related to Ca-rich achondrites (discussed above) since the mesosideritic silicate phases generally are also pyroxene-plagioclase (MASON, 1962; DUKE, 1963). Small amounts of olivine (<2 per cent) are found together with accessory minerals of

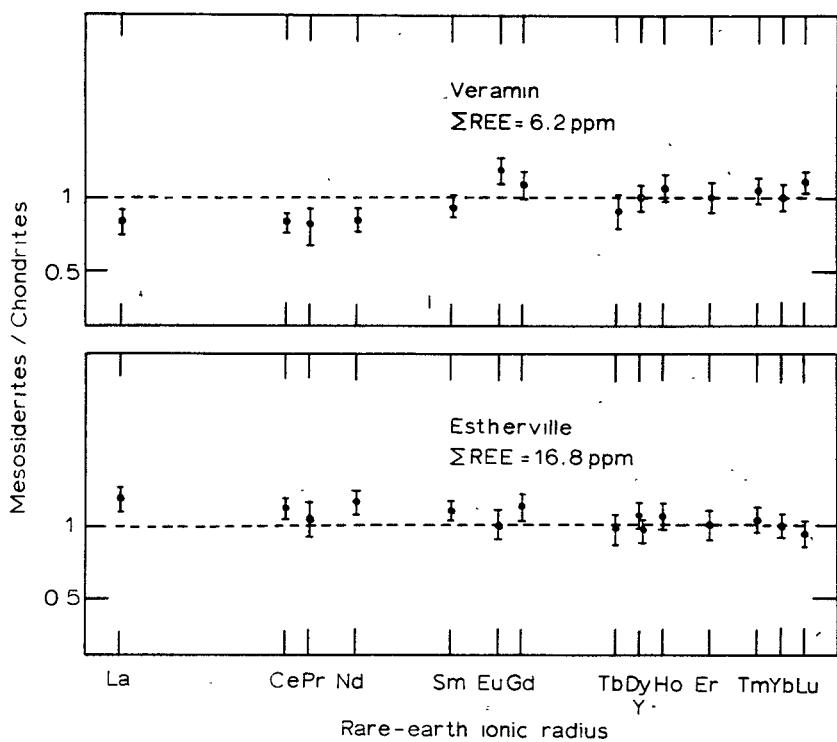


Fig. 5. Comparison plot for mesosiderites (Table 3).

troilite, chromite, schreibersite, apatite and/or merrilite. This general similarity in the mineral phases of Ca-rich (eucritic and howarditic) achondrites and the sporadic occurrence of olivine led PRIOR (1918) to suggest that the mesosiderites were formed by admixture of a pallasitic magma and eucritic magma. LOVERING (1962a) considers the process an invasion of a solid eucritic composition by molten nickel-iron, carrying small crystals of olivine. Both of the above mechanisms seem entirely implausible in view of RE abundances. Since the absolute RE abundances are 11.5 times greater in eucrites than in chondrites, while Veramin and Estherville, respectively, have RE abundances nearly equal to and  $\sim 3$  times greater than RE abundances in chondrites, the consistency of the Prior and Lovering hypotheses requires the removal of  $\sim 90$  per cent of REE to produce Veramin and  $\sim 30$  per cent to produce Estherville, with only  $\sim 10$  per cent average internal fractionation of the REE. To use the argument of dilution of the resultant compound system of eucritic and pallasitic magma also seems unreasonable in view of the small amounts of fragmental olivine. From observations of the textural relations of olivine in mesosiderites, DUKE (1963) also concludes that the LOVERING (1962a) hypothesis with respect to mesosideritic formation is untenable.

A more plausible hypothesis for differences in the formation of the Ca-rich achondrites, mesosiderites, and eucrites and howardites deals with closed, partial, or open systems of fractionation. The large enrichments of the heavy trace elements Sc, Zr, Ba, Th, U, and the REE by a factor of up to ten in eucrites and howardites suggest that eucrites and howardites were relatively open to trace element residuals entering their molten matrices during formation, probably near the surface of a parent body. Mesosiderites such as Veramin must have formed under relatively closed system conditions and those such as Estherville under a partially open system. For an asteroidal-sized body, it is tempting to assign increasing radial positions for Veramin and Estherville, followed by eucritic and howardites achondrites near some surface or interface. The

addition of some molten iron could conceivably heat the mineral system sufficiently to cause a slight internal fractionation of the REE and Sc. Moreover, the problem of synthesis becomes more tractable in light of recent INAA measurements (SCHMITT and SMITH, 1963c). Since the average abundance of Na in the silicate phases of two mesosiderites, Estherville and Vaca Muerta, is  $1530 \pm 170$  ppm as compared with 3050 ppm in ten Ca-rich eucritic achondrites and  $\sim 6500$  ppm in ordinary chondrites, consistency of alkali volatility or diffusivity arguments almost demands a larger integrated temperature-time exposure for the mesosiderites to permit a greater loss of alkalis than in the Ca-rich achondrites. In any case, such fragmentary alkali data do not conflict with the above interpretation for mesosideritic formation. It again becomes apparent that both alkali abundance data and diffusivity measurements of silicates in a considerable suite of meteorites in all meteoritic classes will be of immeasurable help in the elucidation of their formation.

#### Ca-RICH ACHONDRITES (NAKHLITES)

Severe fractionation of the REE and Sc in two nakhlitic meteorites, Lafayette and Nakhla (Ca-rich ( $\sim 15$  per cent CaO) achondrites and observed falls), relative to the REE and Sc in ordinary chondrites (Fig. 3) has been found by SCHMITT and SMITH (1963a). Absolute abundances (Table 3) in Lafayette and Nakhla are nearly identical, and the light REE are about four times more abundant than in ordinary chondrites with comparable amounts of Yb to that found in the average of 20 chondrites. In other Ca-rich ( $\sim 10$  per cent CaO) eucritic achondrites (also observed falls) (Fig. 3), all RE abundances are uniformly 11.5 times greater than in chondrites. Moreover, the Sc fractionation in these nakhlites is reversed with respect to extrapolated trends. For eucritic achondrites, the anticipated Sc fractionation falls approximately on the extrapolated ratio curve of the nakhlitic achondrites. In both the eucritic and nakhlitic achondrites, abundances of Eu have not changed as a result of the complicated

fractionation process. Upon extrapolation of the nakhlitic ratio curve (Fig. 3) back from Yb through Ce, it is seen that the element La has apparently been fractionated relative to the "normal" fractionation process by ~50 per cent; i.e., the expected La ratio of ~6.6 is approximately twice the observed ratio of 3.6. This internal La fractionation has also been observed for many terrestrial rocks (see below).

It seems most significant that the RE distribution pattern closely resembles that observed in many terrestrial basalts (see Figs. 6 and 7). Such similarities in RE fractionation of nakhlites and of terrestrial basalts suggest (SCHMITT and SMITH, 1963a) that nakhlites originated from terrestrial-like volcanic action in or on the meteoritic parent body. This suggestion is supported to some extent by the observations that Nakhla resembles a fine-grained basalt (PRIOR, 1912) and that Nakhla and Lafayette appear mineralogically indistinguishable from each other (MASON, 1963a).

TAYLOR, et al. (1965), have reported very similar O isotopic values for pyroxenes in Nakhla and Lafayette and in ordinary chondrites, and increasing (Fe/Fe + Mg) ratios in pyroxenes of nakhlites relative to ordinary chondrites. These two observations support the hypothesis that nakhlites are differentiation products from parental chondritic matter.

#### Ca-POOR ACHONDRITES

Meteoritic fractionation of the REE and Sc has been found (SCHMITT, et al., 1963, and SCHMITT, SMITH, and OLEHY, 1964) in three Ca-poor achondrites: Norton County, an enstatitic achondrite, and Johnstown and Shalka, two hypersthene achondrites (Table 3 and Fig. 8).

In Norton County, the light REE were depleted monotonically from Gd to La to a factor of ~2.0, with no significant heavy RE fractionation. Also, Eu was depleted by a factor of ~4.0 and both Sc and Y were depleted by ~25 per cent relative to the lanthanides. In its assumed generation from enstatitic chondritic matter (MASON, 1962), Norton County had a

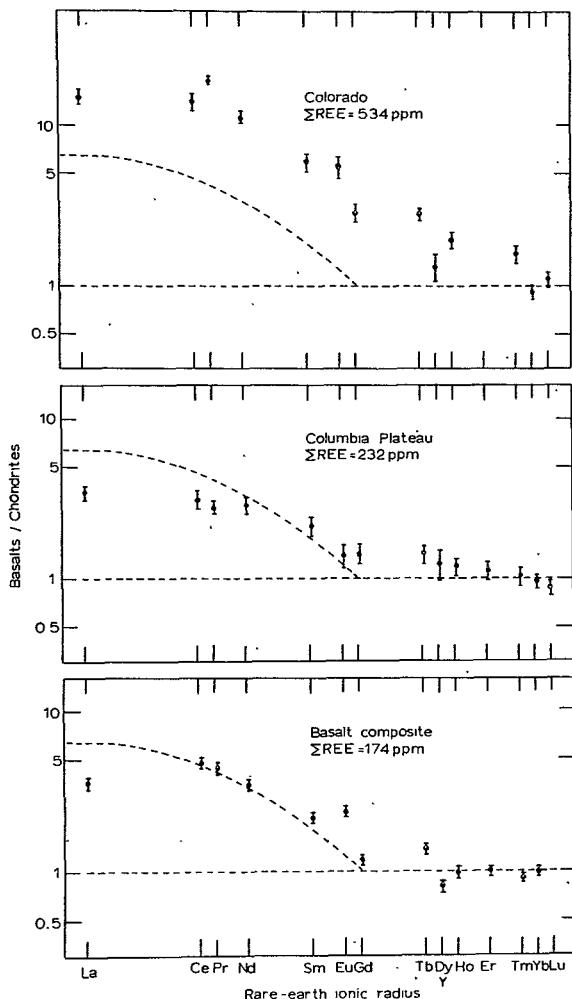


Fig. 6.. Comparison plot for an alkali basalt (Colorado), a continental tholeilitic basalt (Columbia), and a composite of 282 continental basalts (Table 15).

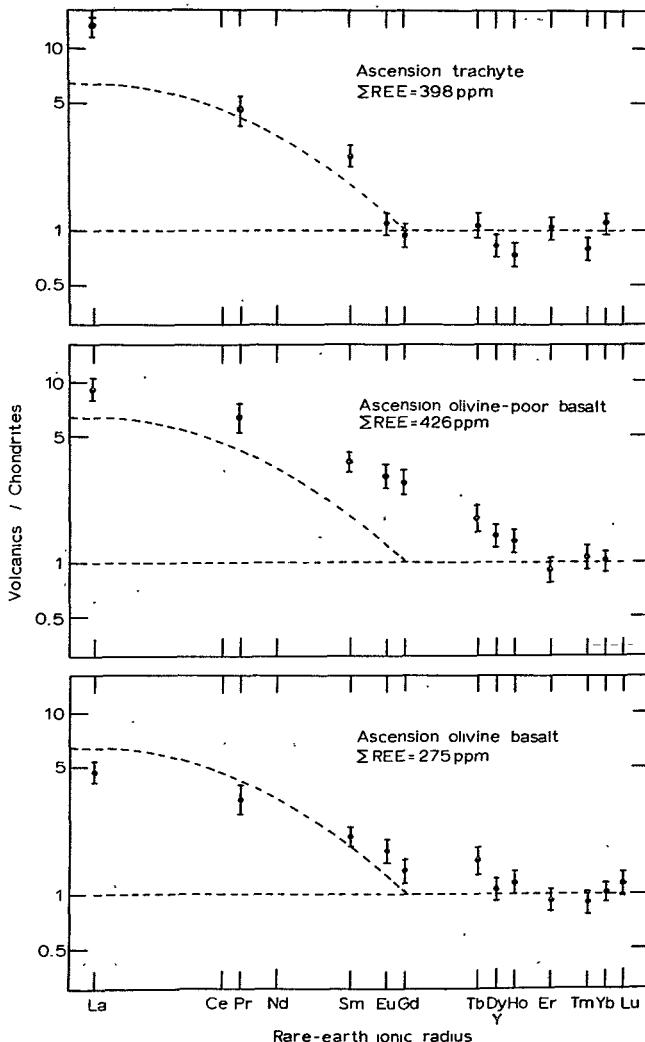


Fig. 7. Comparison plot for Ascension Island volcanic rocks (Table 16).

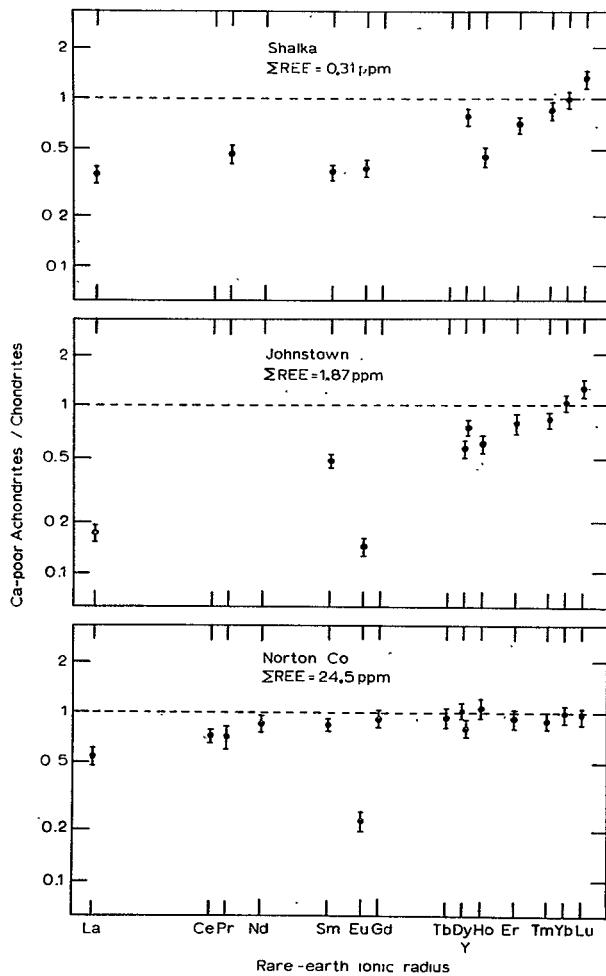


Fig. 8. Comparison plot for Ca-poor achondrites (Table 3).

chemical history involving a period for Eu reduction and fractional loss of only the light REE, since the absolute abundances of the heavy REE and Sc are nearly identical to those in chondrites (Tables 1 and 2).

A period of extreme reduction of Eu to the divalent state during the formation of Norton County and the subsequent loss of Eu (~80 per cent) by diffusion and uptake into other minerals, e.g.,  $\text{Sr}^{+2}$  or  $\text{Pb}^{+2}$  minerals, are compatible with observations made via microprobe analysis (KEIL and FREDRIKSSON, 1963) to the effect that Cu has been reduced to the metallic state, olivine and pyroxene minerals are free of Fe, and Cr, Mn, and Ti are incorporated in sulfide minerals in this particular enstatitic achondrite. Presumably, minerals containing  $\text{Eu}^{+2}$  were then lost from the reducing system.

Since similar  $\text{O}^{18}/\text{O}^{16}$  ratios were observed in pyroxenes from ordinary chondrites, enstatitic chondrites, and achondrites, these meteorites presumably are genetically related (TAYLOR, et al., 1965).

Relative to ordinary chondrites, the element Na has been depleted in Norton County by a factor of ~15; similarly, Pena Blanca Spring, another enstatitic achondrite, had an Na loss of a factor of ~5 (SCHMITT and SMITH, 1963b).

For Yb, a typical non-fractionated heavy REE, an abundance of 0.21 ppm is found in Norton County as opposed to 0.12 ppm in enstatitic chondrites, the assumed parental matter. Since ~20 per cent of enstatitic chondrites are metallic Fe-Ni (UREY and CRAIG, 1953), the calculated Yb concentration in the silicate phase is ~0.15 ppm, or ~33 per cent.

The depletion (more apparent using a linear ordinate scale) of the light REE, Gd to La (Eu is excluded as a special case), in Norton County does not conflict with the suggestion by KEIL and FREDRIKSSON (1963) that the parental enstatitic chondritic matter underwent a rather slow cooling from a melt in the achievement of chemical equilibrium. Such a uniform depletion suggests that the REE may reside in lattice sites, perhaps substituting for  $\text{Ca}^{+2}$  in the oldhamite mineral CaS in Norton County.

Since  $\text{Ca}^{+2}$  has an ionic radius of  $0.98 \text{ \AA}$ , all the REE above  $0.98 \text{ \AA}$  should obviously require less energy for migration, i. e., the energy necessary for La diffusion should be less than that for Gd. On the other hand, all heavy REE (including Y) and Sc have ionic radii less than  $\text{Ca}^{+2}$  and should be readily retained. Sc may be a special case as it resides primarily in the magnesian minerals.

If the REE reside in the predominant magnesian mineral enstatite, a linear fractionation pattern extending uniformly over the entire RE series would be expected, which is contrary to observation. Such an expectation may be partially justified by the apparently large difference in ionic radii between the REE:  $\text{La}^{+3}$ ,  $1.14 \text{ \AA}$ ;  $\text{Lu}^{+3}$ ,  $0.85 \text{ \AA}$ ; and  $\text{Mg}^{+2}$ ,  $0.66 \text{ \AA}$ . Careful RE analyses of individual minerals in these achondrites will help alleviate the present state of confusion.

In Johnstown, a hypersthene achondrite, the absolute content of the light REE La is  $\sim 0.1$  times greater than in chondrites and  $\sim 0.01$  times greater than in the Ca-rich achondrites (Table 3). Figure 8 demonstrates fractionation of the light REE and heavy REE into a possible two-component curve, with the light REE La depleted by a factor of  $\sim 5$ .

For Shalka, another hypersthene achondrite, the absolute La abundance is  $\sim 0.05$  times the La value in chondrites and  $\sim 0.005$  times the La content in the Ca-rich achondrites. The light REE have been fractionated to a lesser degree and the heavy REE to a greater degree than in Johnstown. Both Y and Sc are fractionated more, by a factor of  $\sim 2$ , in Shalka than in Johnstown. No Eu depletion was observed in Shalka. Since degrees of fractionation of the light and heavy REE and also of Sc differ for Shalka and Johnstown, these two achondrites may have been subjected to dissimilar chemical conditions, such as different redox and temperature environments. Single depletion of Eu in the achondrite Johnstown may have occurred through reduction of Eu to the  $+2$  oxidation state. No depletion would be predicted for the element Ce in Johnstown, because in the reduction of  $\text{Eu}^{+3}$  to  $\text{Eu}^{+2}$ , all  $\text{Ce}^{+4}$  is reduced to  $\text{Ce}^{+3}$ , whose chemical properties are like those of the other trivalent REE.

In all the present RE studies, the sample specimens were limited to ~5 g. The presence of large minerals or crystals, especially in achondrites, imposes reservations in the interpretation of abundances in achondritic meteorites. BATE, POTRATZ, and HUIZENGA (1960) reported an abundance of 0.0098 ppm Eu in Johnstown, which agrees well with the 0.0089 ppm value of this work. At least for Johnstown, the depleted Eu content was essentially the same in two samples.

The hypersthene achondrites, eight in total, have been recently discussed by MASON (1963b). In general, this homogeneous group of achondrites have a rather uniform chemical and mineralogical composition, consisting almost entirely of orthorhombic pyroxene ( $26 \pm 1$  per cent  $\text{FeSiO}_3$ ), and also resemble each other in their internal structure. Accessory and trace minerals such as plagioclase feldspar, olivine, chromite, troilite, and nickel-iron in varying quantities are scattered throughout the matrices. Those plagioclase minerals found appear to have uniform compositions of  $\text{Ab}_{15}\text{An}_{85}$ .

The hypersthene achondrites Johnstown and Shalka, whose RE distribution patterns generally appear similar and in an opposite direction to that of Norton County, are apparently genetically related via magmatic differentiation from some common parental material to the basaltic achondrites. This has been inferred (TAYLOR, *et al.*, 1965) from the similarities in the  $\text{O}^{18}/\text{O}^{16}$  ratios of their pyroxene minerals.

For Johnstown, the abundances of the two heavy REE Yb and Lu are nearly equal to those observed in chondritic meteorites, while the light REE, e.g., La, have been fractionated by a factor of ~5 relative to chondritic meteorites. The lithophilic trace elements Sr, Ta, Th, and U have been depleted in Johnstown by ~5, ~3, ~7, and ~7, respectively, relative to ordinary chondritic abundances, and the alkali elements Rb and Cs by ~30 and ~20, respectively (see MASON, 1963b, for references). The similarity between La depletion and depletion of other heavy trace elements with different chemical properties suggests a high temperature

melting process with rather common removal of trace elements such as La, Sr, Ta, Th, and U. Higher volatilities for Rb and Cs in melted silicates probably account for their appreciable deficiency. Note that normal Sc abundances are present in Shalka, and Norton County, and an excess (~50 per cent) is present in Johnstown (Table 3) compared to chondritic abundances. The plotted data of Fig. 8 suggest withdrawal in perhaps two stages of the REE lighter than Yb for both Johnstown and Norton County. It seems coincidental that Eu has been depleted by a similar factor in Johnstown and Norton County; nevertheless, these two achondrites were both subjected to a reducing environment during formation.

The low abundances in Shalka and the two components in the ratio plots (Fig. 8) may be indicative of a two-stage process in their fractionation. The fractionation of the REE and Sc does not seem to indicate any preference for a given formation mode for these achondrites.

REE data for Norton County, Shalka, and Johnstown only provide fragmentary geochemical information for the elucidation of the fractionation histories of these three achondrites. Many more whole rock Ca-poor achondrites and their individual minerals must be analyzed for the REE and other trace elements before any definitive conclusions may be drawn.

#### PALLASITES AND IRONS

Absolute abundances (SCHMITT, SMITH, and OLEHY, 1964) of the REE and Sc in the olivine phase of two pallasites, Thiel Mountains and Brenham, were about 0.05 to 0.3 times the corresponding abundances in chondritic meteorites. The REE and Sc have been fractionated differently in the two pallasites (see Table 4 and Fig. 9). Fractionation of the REE in Thiel Mountains strongly resembles fractionation of terrestrial REE and may (although not likely) be an indication of terrestrial contamination.

LOVERING (1957), using spectrographic techniques, measured trace-elemental abundances in the olivine phase of four pallasitic

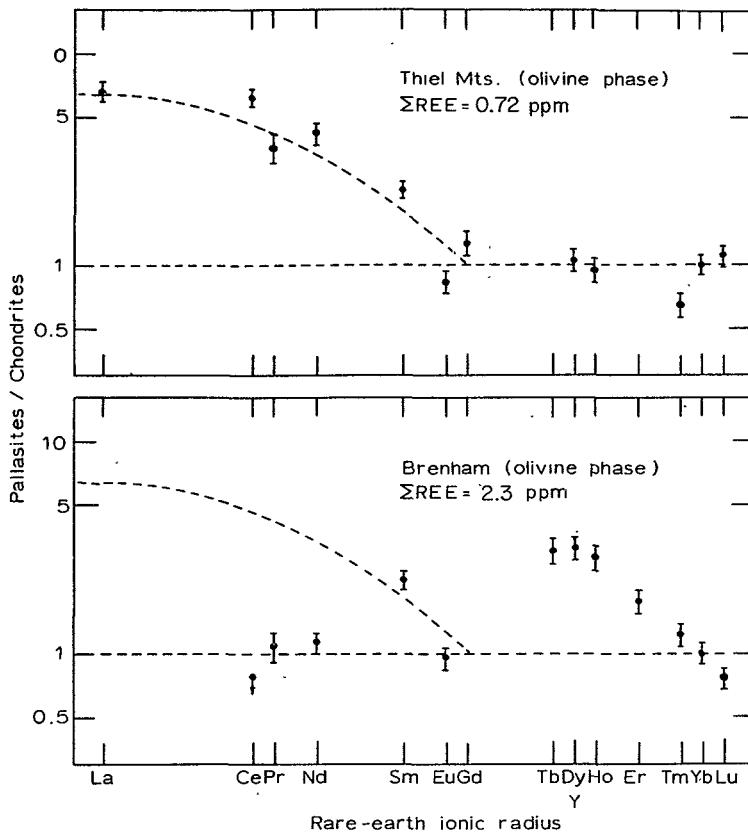


Fig. 9. Comparison plot for pallasites (Table 4). Upper dashed line represents the North American composite shale.

meteorites and found the following mean ppm values: Ba, <1; Co, 35; Cr, 150; Cu, 4; Ga, <2; Ge, <20; Mn, 1900; Ni, 250; Sn, <10; Ti, 25; V, 15; and Zr, <4. Using INAA, SCHMITT and SMITH (1964b) measured the abundances in olivine phases of five pallasites and obtained the following mean ppm values: Na,  $69 \pm 2$ ; Sc,  $1.8 \pm 0.6$ ; Cr,  $320 \pm 110$ ; Mn,  $1970 \pm 260$ ; Co,  $20 \pm 8$ ; Cu,  $33 \pm 6$ ; and Fe,  $10.4 \pm 2.4$  per cent). Considerable reliance may be attached to the spectrographic analyses, since the Co and Cr abundances agree within a factor of 2 with the generally more accurate INAA results. Note the excellent agreement between Mn values and wide difference between Cu values. The above trace element data underscore the fact (MASON, 1963c) that the close-packed structure of olivine allows a minimum substitution of lithophilic trace elements, e.g., ~30 per cent REE and Sc (Brenham), ~4 per cent Ti, ~1 per cent Na, ~20 per cent Sc, and ~10 per cent Cr, in olivine as opposed to a greater substitution of the corresponding abundances in ordinary chondrites. The high Mn concentration of 0.20 per cent in the olivine must be due to the similar geochemical properties of Mn<sup>+2</sup> ( $0.80 \text{ \AA}$ ), Fe<sup>+2</sup> ( $0.74 \text{ \AA}$ ), Mg<sup>+2</sup> ( $0.66 \text{ \AA}$ ).

From the close similarities in Fe/Ni ratios, CRAIG (1953) divided the pallasites into groups and suggested that they represented fractional crystallization stages from material of the two (H and L) chondritic groups (see also CRAIG, 1964, and MASON, 1963c). The two pallasites Brenham and Thiel Mountains, which have similar olivine compositions (12 mole-%  $\text{Fe}_2\text{SiO}_4$ ), belong to the high-iron pallasites and presumably were derived from H-group chondritic-like matter.

Since depletion fractions for lithophilic trace elements in Brenham and Thiel Mountains seem to vary from 1 to 30 per cent, the observed internal fractionation of the REE and Sc relative to chondritic abundances should be not too surprising. Both of these pallasites were finds, and therefore the possibility of terrestrial contamination for both pallasites cannot be entirely ruled out.

Eu seems to be relatively depleted in Brenham by a factor of  $\sim 2$ , which is consistent with a highly reducing environment as discussed in a previous section. Obviously, many more pallasitic meteorites must be analyzed for RE and Sc abundances in order to help clarify any correlations between the pallasites and their genetic relationships to chondrites.

RE abundances observed (SCHMITT, et al., 1963) in the two iron meteorites Odessa and Aroos are  $\sim 10^{-4}$  as great as those observed in chondrites. This agrees well with the corresponding ratios of  $10^{-4}$  found for Th by BATE, POTRATZ, and HUIZENGA (1958), and for Ba and Y by REED, HAMAGUCHI, and TURKEVICH (1958). The small ratio,  $10^{-4}$ , of REE in iron meteorites to a silicate phase is probably attributable to small silicate inclusions present in the iron phase (FISH, GOLES, and ANDERS; 1960).

#### QUALITATIVE SUMMARY OF METEORITIC RE ABUNDANCES

A number of observations have been made about the abundances and isotopic ratios of the trace REE and Sc in various types of meteorites. The most striking result presented is that relative RE and Sc abundances have remained essentially unchanged over the entire chondritic spectrum, i. e., in carbonaceous, bronzitic (H-group), hypersthene (L-group), Soko-Banjitic, and enstatitic chondrites. Since these chondrites may have been subjected to many physicochemical operations, such as recycling of chondritic matter in the meteorite parent body or bodies and through different stages of reduction and metamorphism, some RE fractionation and even fractionation of Sc relative to the REE had been anticipated. In view of the fact that chondrites account for 86 per cent of all meteoritic falls, and assuming that they originate from one or more parent bodies, the near constancy of the relative RE and Sc abundances tends to support the conclusion that the physicochemical history of the meteorite parent body (or bodies) may not have been too complicated, at least in comparison with terrestrial evolution.

Another significant observation concerns the same relative RE distributions in the Ca-rich eucritic achondrites and in chondrites. Both the REE and other lithophilic trace elements with different chemical properties, like Zr, Ba, and U, have been enriched to about the same degree (up to a factor of  $\sim 10$ ) in these basaltic-type achondrites. The fact that no internal RE fractionation occurred in these achondrites was rather surprising because of the rather extensive geochemical reworking that the achondrites have undergone. However, Sc had been fractionated with respect to the REE by about a factor of 2. A plausible process of crystal settling could account for the observed phenomenon, since generally the REE, Ba, and U are concentrated during late crystallizations and Sc is concentrated during early crystallization. Carbonaceous chondritic-like matter may have been the parental material that underwent magmatic differentiation to yield the Ca-rich eucritic achondrites.

Abundances of the REE and Sc must be systematically and accurately determined in a wide variety of separated meteoritic minerals and chondrules in order to elucidate the phenomena of over-all and internal fractionation of this long series of chemical elements. Further understanding of the RE distribution patterns in meteoritic matter will undoubtedly lead to new insights concerning RE distributions in terrestrial and other solar matter.

### REE IN TERRESTRIAL MATTER

The earth's crust consists of a broad diversity of rocks of different ages, compositions, and histories of formation. Its most representative rock types are usually taken to be basalt and granite. It presumably is the complex product of differentiation from the earth's mantle. The rocks of the crust are subject to erosion, decomposition, and differentiation, which form sediments. The sediments, if buried to sufficient depths, may be metamorphosed back to igneous compositions. Fresh igneous material from the mantle has probably added continuously to the crust throughout geologic time.

The REE are separated, or fractionated, by many of the above processes, and it is of interest to examine the RE patterns which result. Because the details of these processes are often obscure, it is worthwhile to see what information about the earth's chemistry can be inferred from observed RE distribution patterns. The number of accurate REE analyses is still so small and the sampling so biased that notions based on RE patterns may be seriously misleading. However, enough data have been accrued to uncover a few apparent regularities, and to compel speculation about the significance and development of RE patterns in several rock types.

It has already been implied in the section on meteorites that there is some monotony of RE patterns among sedimentary rocks, that their general pattern is representative of the earth's crust, and that, relative to chondrites, the crust is enriched in all REE, but especially in the lighter lanthanides, La-Eu. It has also been inferred from the analyses of some basalts that the relative (but not necessarily the absolute) RE abundances of the whole earth may be the same as the RE abundances of chondrites. These speculations will be developed when the pertinent rock types are discussed, but are a convenient guide to hold in mind throughout the presentation which follows.

IGNEOUS AND METAMORPHIC ROCKSUltrabasic Rocks

If the whole earth does have the same relative RE pattern as found in chondrites and, relative to that pattern, the crust is enriched in the lighter lanthanides, then the mantle from which the crust derived must be correspondingly deficient in those elements. A major problem in testing this proposition is that of obtaining samples of material representative of the mantle. Seismic studies, field evidence, and analogies with meteorites suggest that at least the upper mantle may consist largely of peridotite. Peridotitic rocks are found at the surface in various forms, ranging from small nodules in basalts to very large intrusive bodies (TURNER and VERHOOGEN, 1960). The gross compositions of peridotites of all origins are remarkably constant (KUSHIRO and KUNO, 1963). High temperatures and pressures are requisite to their formation and thermodynamic stability, and this suggests an origin in the mantle.

Several investigators defend the hypothesis that the ultrabasic nodules which occur in basalts and kimberlites are fragments of the mantle, torn away and raised to the surface during the intrusion of their host magma (WILSHIRE and BURNS, 1961; NIXON, VON KNORRING, and ROOKE, 1963). The extent of contamination of these nodules with trace elements from the host is not known, but is of potential concern. One peridotite nodule from kimberlite of the Wesselton mine in southern Africa has been analyzed.

Kimberlite itself is peridotitic in composition and, although it is not regarded as representative mantle material, it is of unquestioned deep-seated origin. Three southern Africa kimberlites have been analyzed for REE. Partial analyses of Illinois mica peridotites indicate high RE contents (BRADBURY, 1962).

The rocks of St. Paul's Island, which lies along the mid-Atlantic ridge, consist of mylonitized (badly folded and fractured) peridotite. HESS (1960) has suggested that these rocks may have been part of the oceanic

mantle, now uplifted to the surface. They have been dated by the Rb-Sr method and may be as old as 4.5 billion years (HART, 1964). Three samples of this material have been analyzed for REE.

Ultrabasic intrusions known as alpine-type peridotites occur as steeply inclined lenses or sheets, usually in areas of strongly folded rocks (TURNER and VERHOOGEN, 1960). The mechanism for their emplacement is uncertain, as very high temperatures are required for peridotitic magma, and very little contact metamorphism is found along their boundaries. TURNER and VERHOOGEN (1960) accept as the best hypothesis for their origin the intrusion of crystalline olivine of deep-seated origin, not yet consolidated into a rigid mass, and "greased" by a less-basic residual fluid of significantly lower melting point (BOWEN, 1928). A peridotite apparently of this type has been analyzed by BALASHOV and TURANSKAYA (1962).

Three peridotites which were intruded at high temperatures, as judged from the mineral assemblages and large contact metamorphic aureoles, have been analyzed for REE. The mineral assemblages of these peridotites are those expected for the mantle, according to RINGWOOD (1962a, b), GREEN and RINGWOOD (1963), and GREEN (1964).

Of course, it cannot be said with certainty that any of the materials discussed here is unaltered mantle matter, or that none is contaminated with trace elements as a result of contact with crustal material during ascent. Nevertheless, there are many reasons why some or all of them might be fragments of the mantle, and it is from this standpoint that they have been tentatively interpreted (FREY and HASKIN, 1965). The results of the analyses are presented in Table 13, and patterns representative of the group are shown in Figs. 10 and 11.

Of the specimens analyzed, only the high temperature peridotites have RE patterns which are complementary to that of the crust (Fig. 10). These three samples are similar both in relative and absolute RE abundances.

Table 13. RE<sup>a</sup> Contents of Peridotites (ppm)<sup>a</sup>

Element	Alpine, Polar Urals <sup>b</sup>	Nodule, Wesselton Mine <sup>c</sup>	High Temperature Intrusions			St. Paul's Islands			Kimberlite		
			Tinaquillo, Venezuela <sup>d</sup>	Lizard, Cornwall <sup>d</sup>	Mt. Albert, Quebec <sup>d</sup>	PH-1 <sup>d</sup>	PI-1 <sup>d</sup>	H-2 <sup>d</sup>	Premier <sup>d</sup>	Mwadui <sup>d</sup>	Dutoitspan <sup>c</sup>
La	1.8	3.3	0.0041	0.0046	0.0067	4.5	4.6	0.58	26	26	200
Ce	3.3	8.0	0.107	0.059	0.054	9.3	18.7	0.57	---	72	510
Pr	0.60	1.02	0.017	0.00111	0.0031	1.76	2.6	0.078	9.0	6.6	36
Nd	2.4	3.4	0.20	0.042	0.042	6.2	8.0	0.31	24	40	134
Sm	0.88	0.57	0.113	0.033	0.0090	1.11	1.7	0.095	7.0	5.6	11.6
Eu	----	0.16	0.068	0.017	0.0059	0.32	0.58	0.53	2.0	1.39	0.28
Gd	0.90	0.65	0.27	0.071	0.047	1.16	2.5	0.19	5.2	8.9	5.3
Tb	0.19	0.09	0.079	0.081	0.038	0.31	0.33	0.047	0.58	---	---
Dy	0.95	0.59	----	----	----	----	----	----	----	----	----
Ho	0.24	0.14	0.095	0.052	0.022	0.18	0.23	0.045	0.67	---	0.63
Er	0.47	0.36	0.27	0.17	0.081	0.53	0.70	0.13	0.87	---	1.38
Tm	----	0.05	0.049	0.030	0.0149	0.068	0.086	0.027	----	0.22	0.22
Yb	0.57	0.43	0.45	0.27	0.17	0.50	0.57	0.16	0.96	1.18	1.20
Lu	3---	0.06	0.031	0.021	0.0148	0.072	0.047	0.022	---	0.19	0.16
Y	4.8	----	2.1	1.21	0.54	5.0	5.0	1.24	4.9	7.3	12.9
ΣREE	17	24	3.9	2.1	1.07	32	48	3.7	136	180	910

<sup>a</sup>In Tables 13 through 40, all experimental values with digits to the right of the decimal point greater than 150 have been rounded off to the second significant number.

<sup>b</sup>BALASHOV and TURANSKAYA (1962).

<sup>c</sup>SCHMITT, et al. (1963).

<sup>d</sup>FREY and HASKIN (1965).

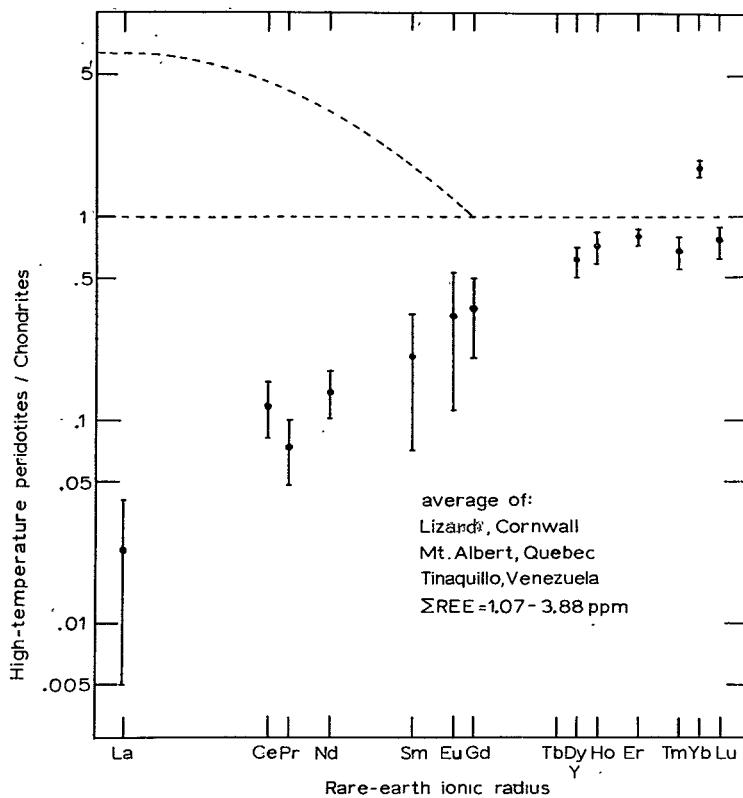


Fig. 10. Comparison plot for high temperature peridotites (Table 13). Upper dashed line represents the North American composite shale.

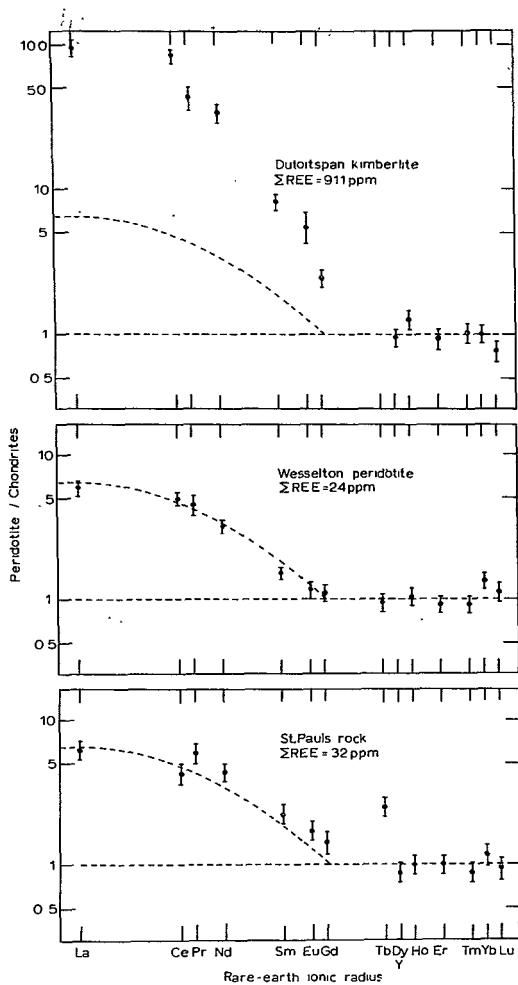


Fig. 11. Comparison plot for peridotitic materials (Table 13). Upper dashed line represents the North American composite shale.

FREY and HASKIN (1965) considered some possible consequences if the high temperature peridotites were a representative average of the upper mantle. They assumed that the RE pattern of the earth's crust was represented by the sediment distribution and from analyses of crustal rocks estimated the range inside which the absolute crustal contents of these elements would lie. They further assumed that the relative (but not the absolute) RE concentrations for the mantle plus crust would be the same as found in chondrites. They then calculated the quantity of high temperature peridotite with its light-lanthanide depleted RE pattern which would be left behind as mantle if the crust had developed from it. The mass of the peridotite required exceeded the actual mass of the mantle by nearly two orders of magnitude. This calculation simply shows that the high temperature peridotite cannot be representative of the entire mantle. If the above two assumptions are essentially valid, the mantle has to be, on the average, more concentrated in REE and/or relatively less depleted in the lighter lanthanides. If the high temperature peridotites are taken to represent only the upper mantle, then the extent of RE differentiation would decrease with depth in the mantle, and the lower mantle would be more primitive in its composition than the upper portion (Fig. 12).

The rest of the peridotites correspond to an upper mantle which would be relatively enriched in lighter lanthanides, as is the crust (Fig. 12), since relative enrichment in the light lanthanides is probably a result of partitioning which is accompanied by an increase in absolute concentration. The mantle would be most fractionated and depleted in REE in its deepest interior, just the opposite of the conclusion reached above. The RE patterns and contents are consistent with a partitioning of the type described, because the extent of light lanthanide enrichment is directly proportional to the absolute concentration of REE in the peridotites. This is illustrated in Fig. 13, where the La/Y ratio, as a measure of the relative light lanthanide enrichment, is plotted against total RE concentration. Such a relationship would not be expected if crustal contamination were the source of the REE. A point which represents chondritic meteorites is included. The points for kimberlites

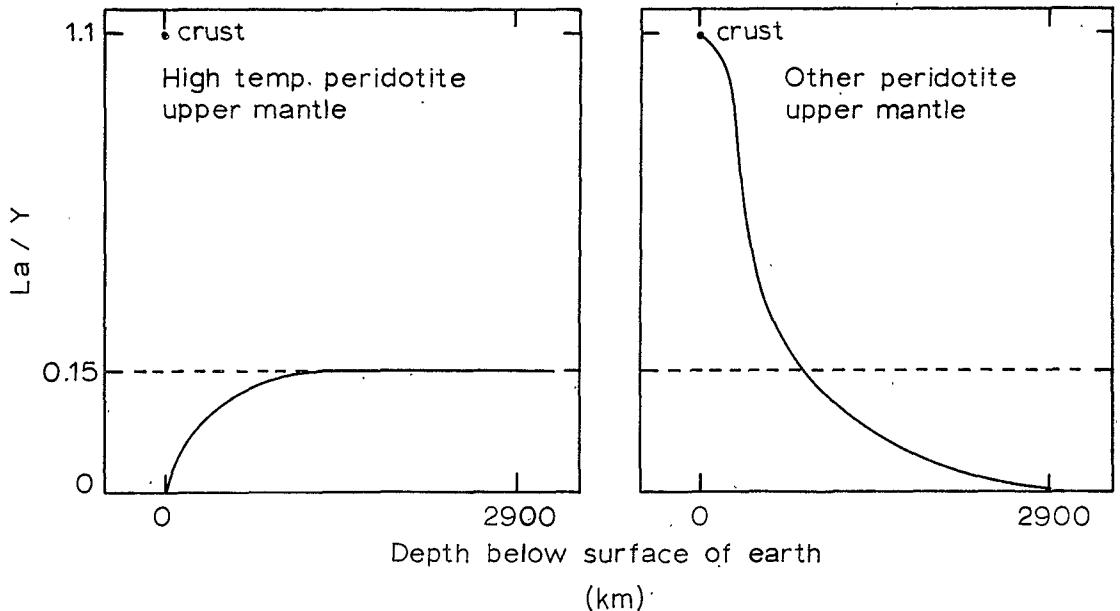


Fig. 12. Qualitative trend of the La/Y ratio plotted as a function of depth for a mantle with a RE pattern similar to that of high temperature peridotites (left side) or that of other peridotites (right side).

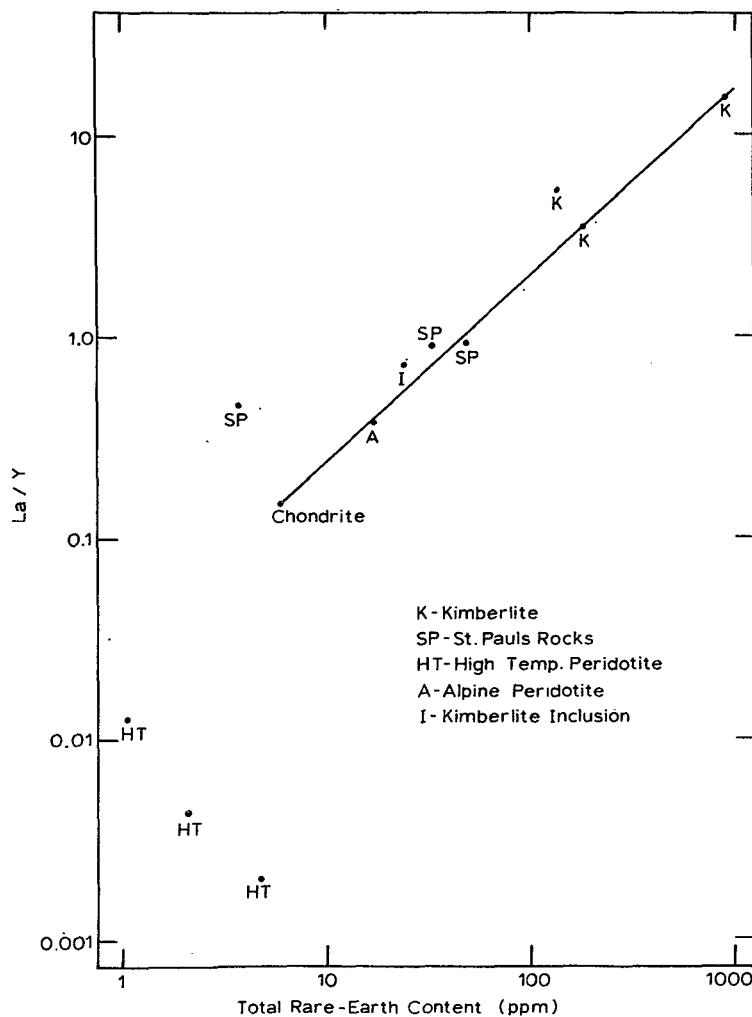


Fig. 13. La/Y ratio for peridotitic materials plotted against total RE content. The points for materials with higher absolute RE contents than chondritic meteorites lie on a line.

also fall on the line, even though kimberlites are not normally considered to be genetically related to peridotites. It is intriguing to note that the relationship holds only for those peridotitic materials with absolute RE contents greater than those of chondritic meteorites, and that the point for chondrites falls on the line. The absolute RE contents of crustal material are compatible with development of the silicate portions of the earth from matter with the RE concentrations found in chondrites, as will be shown later. No definite conclusions regarding the composition and structure of the mantle are possible until the relationship of the peridotites to the mantle is better understood. None of the peridotites examined seems likely to be unaltered primordial terrestrial material, nor does any appear to represent the average composition for the present mantle. This is emphasized by the radioactive elemental contents of peridotites, which are too low to account for the heat flow in oceanic areas (TILTON and REED, 1963).

#### Basic Rocks

Other materials which, according to volcanic and seismic studies, have their origin in the upper mantle are the basalts. These, plus their coarser grained compositional equivalents, the gabbros and diabases (dolerites), are presumed to be the predominant rock of the oceanic crust and are major constituents of the continental crust. Basalts show relatively little variability in gross chemical composition; a number of types have been recognized on the basis of differences in composition and mineralogy. The principal basalt classes are alkali-olivine and tholeiitic, based on whether the rock in question has normative nepheline or normative quartz, respectively. High alumina content or geographical environment is sometimes stressed. The various classes are distinct only in definition, however, and the members of each class grade smoothly into those of the adjacent ones.

The origin of basalt is frequently attributed to partial melting in the mantle of material of peridotitic composition, but the details remain obscure. In an involved laboratory study of many natural and synthetic basalts and eclogites, YODER and TILLEY (1962) concluded that these materials were, by the nature of their melting curves, derivatives of a more primitive source. They determined that, at the presumed depths of

basalt magma generation, the mineral phases of the compositionally equivalent eclogites would be the stable ones. They showed that variations in magma composition would arise from different pressure-temperature conditions for partial melting of the parent material, and that this, plus crystal settling at depth, would affect the composition of the material reaching the surface. High pressures would favor alkali basalt formation and low pressures would favor tholeiite. Crystal settling of garnet would favor alkali basalt, and similar removal of omphacite, the other principal mineral of eclogite, would leave a liquid of tholeiitic composition. Yoder and Tilley did not require a world-encircling peridotite shell in the upper mantle, as is sometimes postulated, nor did they reject it.

KUSHIRO and KUNO (1963) outlined the production of tholeiitic, alkali, and high alumina basalts from peridotite on the basis of depth of origin (pressure). They calculated that partial melting of 2-9 per cent of peridotitic material would provide the observed composition of basalt. The mineralogy of the residue would remain that of peridotite.

O'HARA (1965) argued that the melting behavior of basalts does not show that they are the initial direct products of partial melting of a single source material. Rather, a continued differentiation following the first partial melting seems to be required. He stated that the immediate products of partial melting of peridotite at high pressures, under wet or dry conditions, would not resemble basalt in composition. There appears to be no known or predictable set of environmental conditions by which nepheline-normative (alkali) basalt can be obtained from a magma of tholeiitic composition. He pointed out that the depth of partial melting could determine the compositions of extrusive lavas only if the lavas were brought swiftly to the surface, which does not seem to be the case for natural basalts. O'Hara outlined a model which provides for compositional variation both from the conditions of partial melting and from varying degrees of fractional crystallization during slow and interrupted ascent of the liquid products to the surface.

The results of RE analyses for basalts and gabbros appear in Tables 14-17 and in Figs. 6, 7, 14-16. In terms of their RE patterns, these rocks split so far cleanly into two distinct groups: oceanic tholeiites and all others.

The oceanic tholeiites have RE distribution patterns more nearly like those of chondrites than do any other materials of terrestrial origin examined thus far (FREY and HASKIN, 1964; FREY, HASKIN, and POETZ, 1965). Only La, Ce, and Pr were found to be fractionated measurably away from the chondritic pattern and, unlike most crustal materials, they were depleted, as shown in Fig. 14. The close approach of the oceanic tholeiitic distributions to the chondritic pattern was cited as a strong argument for a whole earth chondritic relative abundance distribution for the REE.\*

The oceanic tholeiitic average RE content of 102 ppm is 17 times that of chondrites and nearly twice that of the Ca-rich achondrites. This further emphasizes the fact that there have occurred considerable changes in the gross composition of matter which have concentrated the REE as a group, but which have only slightly affected their relative abundances.

The compositions and petrology of this very homogeneous group of basalts has been studied in detail by SHAND (1949), ENGEL and ENGEL (1963, 1964a, b) and MUIR, TILLEY, and SCOON (1964). They have no

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\* Of the elements Nd-Lu and Y, only Y, Tb, and Tm are not statistically alike in the two materials within one standard deviation of  $\sim \pm 7$  per cent, from an assumed  $\sim 5$  per cent uncertainty in the chondrite and the oceanic tholeiite averages. Since standard deviations are being used, only 2/3 of the error bars need cross the line for the samples to be identical. It was noticed during the writing of this paper that the Tb values of the Wisconsin and Russian analysts are consistently relatively higher than those of the California group, suggesting a systematic error for that element in chondrites. An intercalibration experiment by the authors of the present paper showed that the reported Tb contents of the chondrites may be 18 per cent too low, so the position of Tb in Figs. 2 and 14, and in other figures where it is well above the lines, is not an indication of anomalous behavior for that element. Y is also lower in the terrestrial samples, probably outside experimental errors, and whether this indicates a systematic error or a real difference is at present unresolved.

Table 14. RE Contents of Oceanic Tholeiitic Basalts (ppm)

	Mid-Atlantic Ridge					East Pacific Rise	
	GE 159 <sup>a</sup>	GE 160 <sup>a</sup>	GE 260 <sup>a</sup>	D-2-1 <sup>b</sup>	D-3 <sup>b</sup>		
						Guadalupe <sup>a</sup>	Mendocino <sup>b</sup>
La	4.5	3.0	5.0	5.0	6.2	1.9	4.7
Ce	18	18	---	11.8	---	13.9	13.0
Pr	2.1	2.5	2.4	2.1	2.7	1.9	4.0
Nd	13.2	13.5	14.0	9.7	20	8.6	19
Sm	4.4	4.8	4.4	4.3	6.6	2.8	5.6
Eu	1.8	2.1	1.9	1.7	1.90	1.35	2.1
Gd	6.5	8.4	7.3	5.5	7.1	4.6	10.4
Tb	1.25	1.27	1.7	1.19	1.47	0.83	1.6
Dy	---	---	---	---	---	---	---
Ho	1.7	2.1	1.40	1.5	1.8	1.06	2.1
Er	4.7	5.8	---	3.9	5.3	3.3	6.1
Tm	0.79	0.83	1.18	0.56	0.76	0.41	1.00
Yb	4.0	4.0	4.2	3.0	4.5	2.8	5.2
Lu	---	0.92	0.79	0.52	---	0.57	---
Y	34	47	34	33	47	30	50
$\Sigma$ REE	97	114	100	84	117	74	126

<sup>a</sup>FREY and HASKIN (1964).<sup>b</sup>FREY, HASKIN, and POETZ (1965).

Table 15. RE' Contents of Basalts (ppm)

	Columbia Plateau <sup>a</sup>	Linz, Prussia <sup>b</sup>	Montana Pillow Lava <sup>b</sup>	Jefferson Co., Colo. <sup>b</sup>	Composite of 213 <sup>b</sup>
La	25	41	----	79	17
Ce	66	140	98	210	66
Pr	7.9	13.5	13.6	40	8.5
Nd	37	57	55	105	32
Sm	10.0	9.7	17	20	6.9
Eu	2.3	3.6	3.8	6.6	2.7
Gd	10.2	8.8	12.6	14.5	5.9
Tb	1.7	1.44	2.3	2.3	1.08
Dy	9.6	----	----	----	----
Ho	1.9	1.47	3.30	2.3	1.11
Er	5.4	3.1	4.2	----	3.3
Tm	0.75	----	0.53	0.81	0.44
Yb	3.9	3.5	2.6	2.6	2.7
Lu	0.64	0.61	0.49	0.57	----
Y	53	26	30	41	25
$\Sigma$ REE	230	310	290	530	170

<sup>a</sup>SCHMITT, SMITH, and OLEHY (1964).<sup>b</sup>FREY, HASKIN, and POETZ (1965).

Table 16. RE Contents of Oceanic Island Volcanics (ppm)

	Gough Island			Ascension Island			Hawaii
	Olivine-poor Basalt <sup>a</sup>	Trachy-andesite <sup>a</sup>	Trachyte <sup>a</sup>	Olivine Basalt <sup>a</sup>	Olivine-poor Basalt <sup>a</sup>	Soda Trachyte <sup>a</sup>	Kilauea Basalt <sup>b</sup>
La	47	115	200	38	67	83	10.5
Ce	----	----	----	----	----	----	35
Pr	14.2	7.3	54	10.7	19	11.7	3.9
Nd	----	----	----	----	----	----	18
Sm	15	15.0	24	11.1	18	11.0	4.2
Eu	4.3	4.9	0.65	3.4	5.4	1.7	1.30
Gd	9.0	12.3	21	11.3	21	6.3	4.7
Tb	1.17	----	3.9	2.0	2.1	1.13	0.66
Dy	----	----	----	----	----	----	3.0
Ho	1.38	1.48	4.1	2.2	2.3	1.12	0.64
Er	2.8	3.9	12.1	5.2	4.6	4.6	1.7
Tm	----	0.41	1.7	0.73	0.80	0.52	0.21
Yb	3.0	3.5	8.5	4.6	4.3	4.0	1.11
Lu	----	----	----	0.94	----	----	0.20
Y	30	38	101	56	67	34	---
$\Sigma$ REE	280	640	1,040	280	430	400	95

<sup>a</sup>FREY, HASKIN, and POETZ (1965).<sup>b</sup>SCHMITT, et al. (1963).

Table 17. RE Contents of Gabbros and Diabases (ppm)

	Gabbros			Diabases			
	Ironton, Mo. <sup>a</sup>	Bushveldt <sup>a</sup> (Norite)	San Marcosh <sup>b</sup>	W-1 <sup>c</sup>	W-1 <sup>d</sup>	Finnish <sup>e</sup> (Gabbro and Diabase)	Finnish <sup>f</sup>
La	12.8	4.8	4.0	9.3	11.7	1.7	34
Ce	--	6.4	14.5	15	24	3.4	85
Pr	4.7	1.37	2.2	3.5	3.7	0.86	15
Nd	20	4.3	7.7	20	15	4.3	81
Sm	5.9	1.08	2.2	3.5	3.8	0.86	39
Eu	3.7	0.59	1.05	1.29	1.09	--	10
Gd	5.1	1.04	--	--	4.2	1.6	43
Tb	0.50	--	0.48	0.81	0.75	--	10
Dy	--	--	2.8	4.4	--	0.87	48
Ho	1.21	0.23	0.57	0.86	1.35	--	--
Er	4.4	0.81	--	--	2.6	0.88	30
Tm	0.72	0.10	0.25	0.33	0.36	--	8.8
Yb	2.7	0.54	1.70	2.2	2.1	~0.8	32
Lu	0.60	--	0.26	0.35	0.33	--	11
Y	26	6.2	16	28	24	4.7	--
$\Sigma$ REE	123	28	59	96	100	22	--

<sup>a</sup>FREY, HASKIN, and POETZ (1965).<sup>b</sup>TOWELL, VOLFOVSKY, and WINCHESTER (1965).<sup>c</sup>TOWELL, WINCHESTER, and SPIRN (1965).<sup>d</sup>HASKIN and GEHL (1963a).<sup>e</sup>SAHAMALA (1945).<sup>f</sup>SAHAMALA and VÄHÄTALO (1941); relative, not absolute, values are given.

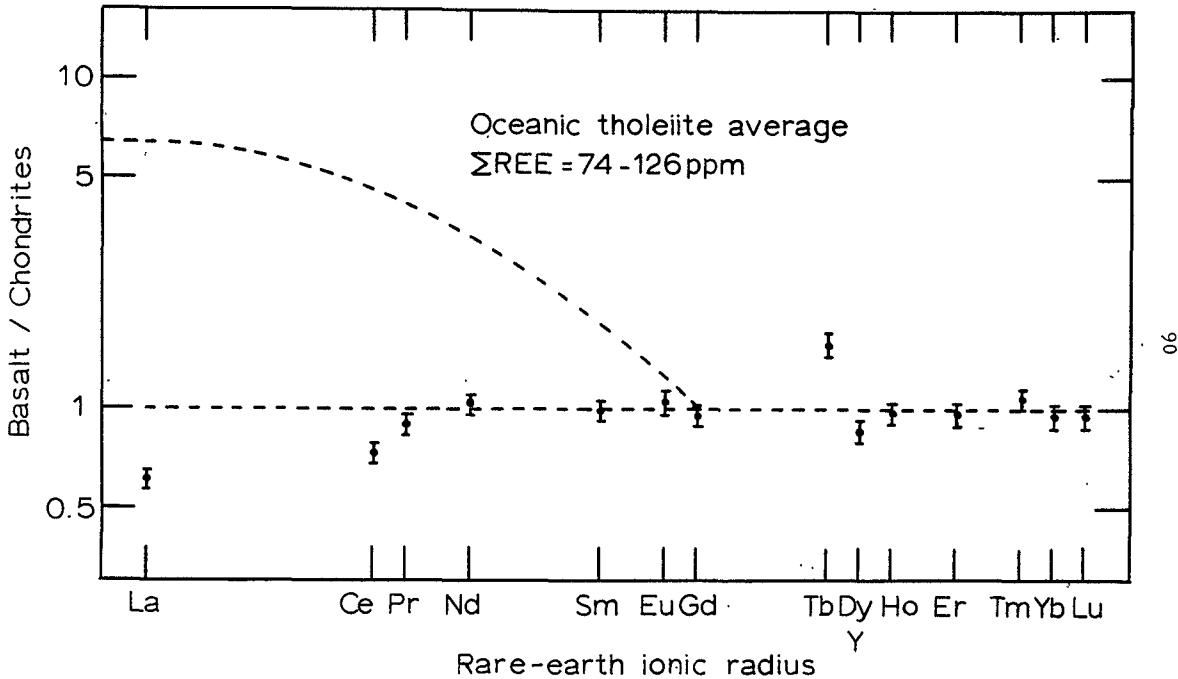


Fig. 14. Comparison plot for the average RE pattern of seven oceanic tholeiitic basalts (Table 14). Upper dashed curve represents the North American composite shale.

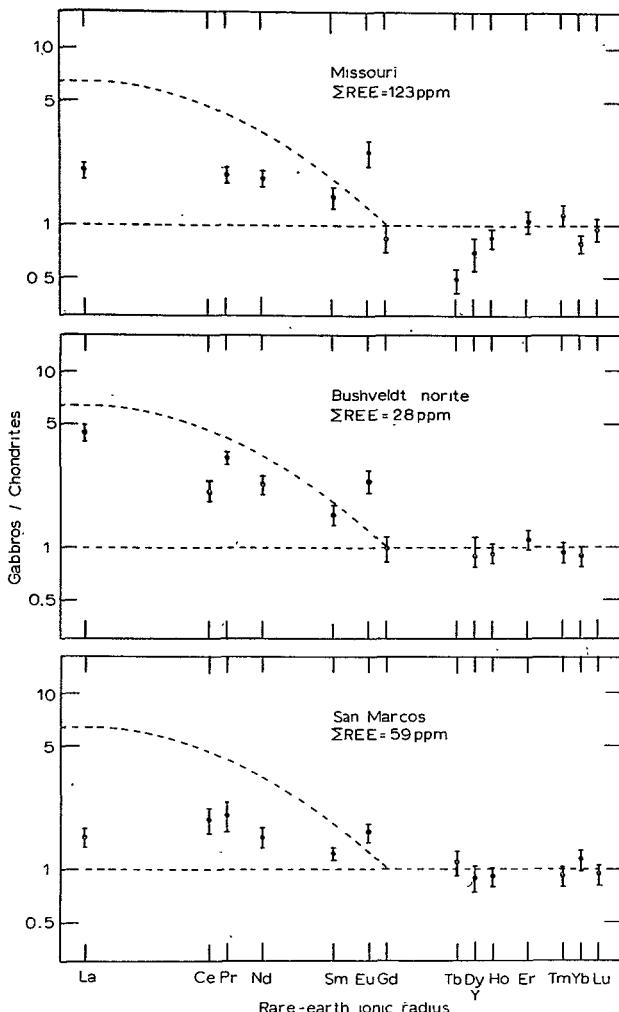


Fig. 15. Comparison plot for gabbros (Table 17). Upper dashed curve represents the North American composite shale.

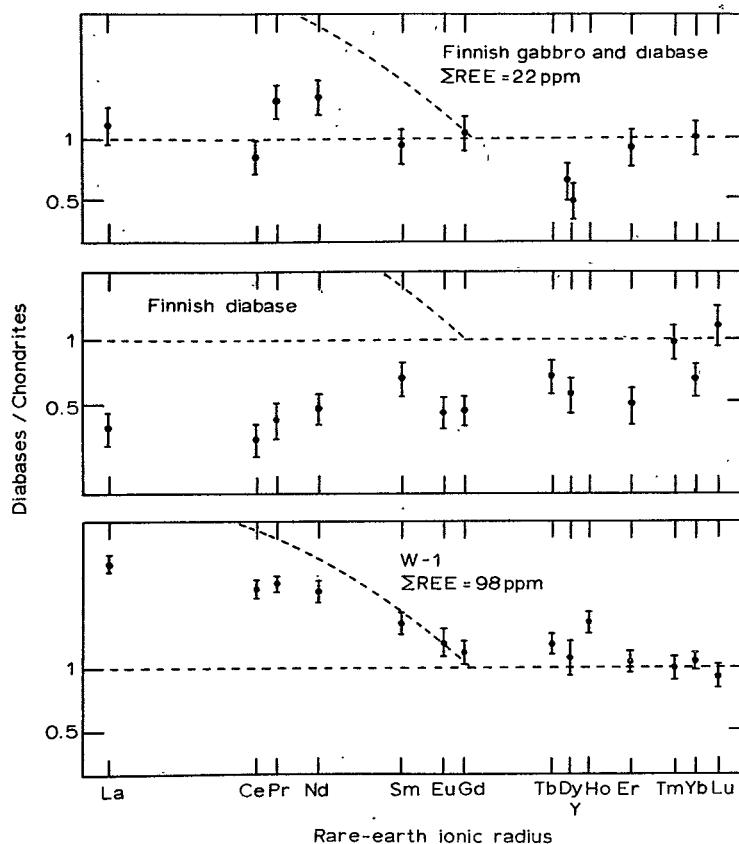


Fig. 16. Comparison plot for diabases (Table 17).

mineralogical features which serve to distinguish them from all other tholeiitic basalts. Their gross chemical compositions are nearly identical with those of other tholeiites, except that they tend to be lower in  $K_2O$ . Other than potash content and RE patterns, only the site of their occurrence serves to set them apart from other basalts. Their occurrences have been summarized by ENGEL and ENGEL (1964a, b), who concluded that they are the overwhelmingly predominant volcanic basalt associated with the mid-Atlantic ridge, the east Pacific rise, and the Indian Ocean counterpart. The Engels further suggested that they may be the principal basalts of the entire oceanic regions, and possibly the only magma extruded by the mantle itself. In fact, the uniformity of oceanic tholeiites led the Engels to postulate that those rocks might be a complete, rather than partial, melt of the mantle. In view of the complexities described earlier regarding the origin of basalts, these intriguing suggestions should be approached with caution. Nevertheless, the uniformity of composition of these rocks and their nearly chondritic RE patterns may indicate a simple derivation from the mantle. The oceanic tholeiites are found in submerged regions along the ridges, but the oceanic islands and tops of seamounts associated with these features are characterized by alkali basalt. The alkali basalt appears to be at least  $10^3$  times less abundant than oceanic tholeiite in this region. This has led the Engels to suggest that alkali basalt has tholeiite as its parent.

An example of the most common type of tholeiitic basalt, flood or plateau basalt, is the Columbia plateau sample of Fig. 6. The RE patterns of this rock follow the same general trend of light RE enrichment as is displayed by the alkali basalts and most other crustal materials. That pattern, another of a representative alkali basalt, and one for a composite of 282 continental basalts from around the world are shown in Fig. 6. The number of analyses is scarcely adequate to constitute a comprehensive survey of basalt in RE patterns, but some regularities have been listed (FREY, HASKIN, and POETZ, 1965). These are stated below, and apply to all basalts examined except the oceanic tholeiites.

As was observed for peridotites, basalts with the highest total RE concentrations tend to be the most enriched, relative to chondritic meteorites, in the lightest lanthanides. This relationship is much more approximate for these rocks than it is for the peridotites, and becomes still more approximate for more acid rocks. There seems to be, for the basalts, some variability among La, Ce, and Pr as to which is the most strongly enriched relative to chondrites. In some of the patterns, the extent of enrichment is about the same for all three. In others, La clearly predominates. In still others, La is definitely less enriched than Ce and Pr, and this includes the composite sample. Rarely in basalts is La as abundant relative to Ce and Pr as it is in sedimentary rocks. Also, unlike the sediment RE pattern, fractionation among the heavier lanthanides and Y is common for basalts. Relative enrichment in basalt patterns over chondrites becomes apparent for all the heavier lanthanides down to Yb, which is used for pattern normalization. However, in the composite basalt, which hopefully represents a good average, relative enrichment of the lanthanides heavier than Gd is slight, if it exists at all.

No significant pattern differences were found between the continental basalts and the alkali basalts of Gough and Ascension Islands (Table 16, Fig. 7), even though these islands lie on the mid-Atlantic ridge, which is a source of oceanic tholeiite. FREY, HASKIN, and POETZ (1965) considered their RE patterns in the light of the suggestion of ENGEL and ENGEL (1964b) that they might have derived from oceanic tholeiitic compositional material. Without regard for mechanism or chemical features other than composition, it was supposed that island alkali basalts, with their light-lanthanide-rich patterns, and the oceanic tholeiites, which are slightly depleted in the light lanthanides, are differentiates of some precursor which was suitably rich in RE content but had a chondrite-like relative RE distribution. (The Ca-rich achondrites are evidence that such a precursor can arise from natural processes.) The approximate ratio of alkali basalt to oceanic tholeiite needed to produce the hypothetical

precursor was found to be 5/95. Addition of the gross compositions of these materials gave a composition for the precursor which was effectively the same as that of the oceanic tholeiite. Thus, the RE data were shown to be compatible with the Engels' hypothesis.

It was also shown by FREY, HASKIN, and POETZ (1965) that the relatively rare, more acid trachyandesites and trachytes of Gough and Ascension Islands have RE patterns consistent with their derivation by further differentiation of alkali basalt magma, as seen from the results in Table 16 and Fig. 7.. These rocks have absolute RE contents which are quite high compared with those of their suggested parent material and those of continental acid rocks.

The absolute RE contents of the continental and island basalts range from 95 to 534 ppm. The average RE content would be best obtained from the composite basalt, which has 174 ppm. The composite basalt contains 2.7 ppm Yb, the range for continental basalts is 1.1-4.6 ppm, and the average for oceanic tholeiites is 4.0 ppm. The oceanic tholeiites, while relatively lower in total RE content (104 ppm), are relatively enriched by about 40 per cent in the heaviest lanthanides.

In at least three of the nine continental and island basalts, Eu was enriched relative to its neighbors Gd and Sm by 40-60 per cent, supposedly because of reduction to the +2 state.

For the coarser grained diabases and gabbros there are very few data. The available analyses are included in Table 17 and are displayed in Figs. 15 and 16. The absolute RE contents are lower than in the basalts, ranging from 22 to 123 ppm. This might occur because slower crystallization would enable more exclusion of the REE from the crystallizing minerals and their diffusion out of the main rock mass. However, the RE patterns, while noticeably enriched in the lighter lanthanides over chondrites (except possibly for the Finnish gabbro and diabase) are not nearly as much enriched in over-all RE content. This suggests that these coarser grained rocks have not been quite as highly differentiated as the basalts by processes

such as crystal settling or solidification and partial remelting, which seem to concentrate the REE in the liquid phases and to fractionate them strongly. Relative enrichment of Eu over Sm and Gd to the extent of 1.3 to 3 times is found in three of the specimens.

Equivalent in gross composition to basalt is eclogite, whose mineral assemblage is stable at higher pressure-temperature conditions than basalt. Like peridotite, eclogite has mechanical properties compatible with seismic requirements for the upper mantle. YODER and TILLEY (1962) show that eclogite, not basalt, would be the stable mineral association from partial melting of material at the depth of the upper mantle. On petrologic grounds, peridotite is a superior choice as the major constituent of the upper mantle; at least, the incidence of eclogite as inclusions in basalt and kimberlite is much lower than that of peridotite (KUSHIRO and KUNO, 1963; NIXON, VON KNØRRING, and ROOKE, 1963).

Analyses have been reported for four eclogites: two from kimberlite pipes, southern Africa; one from a basic breccia pipe, Delegate, Australia; and one out of a large inclusion in dunite, Shikoku, Japan. The Delegate specimen has been claimed by LOVERING (1962b) to be an unaltered sample of mantle material, with a possible Rb-Sr age of  $4.3 \pm 0.2$  billion years. He suggests that trace element contamination of the Delegate specimen is less likely than for the African materials. The results of the four analyses appear in Table 18, and RE patterns are compared with chondritic patterns in Fig. 17.

All the eclogite RE patterns appear to be at least slightly fractionated away from the chondritic pattern, but except for the Dutoitspan specimen, the variations from chondrites are less than a factor of 2. This has been cited as further evidence of a chondritic whole earth RE relative abundance distribution (FREY and HASKIN, 1965). There was considerable concentration of the REE in these materials with relatively little alteration from the chondritic pattern. This is reminiscent of the observed RE enrichment of the Ca-rich achondrites and the oceanic tholeiitic basalts. The Dutoitspan specimen was extracted from kimberlite with a RE content of

Table 1.8. RE Contents of Eclogites (ppm)

	Delegate <sup>a</sup>	Roberts Victor <sup>b</sup>	Dutoitspan <sup>c</sup>	Japan <sup>c</sup>
La	3.6	4.2	7.4	1.8
Ce	14.1	9.7	37	9.5
Pr	2.5	1.6	5.4	0.70
Nd	11.7	5.6	20	3.4
Sm	3.8	1.49	4.9	1.45
Eu	1.25	0.46	1.44	0.70
Gd	5.2	1.7	4.7	2.1
Tb	0.75	0.25	0.75	0.32
Dy	5.7	≤2.3	----	---
Ho	1.00	0.45	1.33	0.39
Er	2.8	1.6	2.9	1.11
Tm	0.41	0.22	0.46	0.14
Yb	2.0	1.6	2.3	1.13
Lu	0.32	0.26	----	0.16
Y	27	8.8	23	9.2
ΣREE	82	40	116	34

<sup>a</sup>SCHMITT, SMITH, and OLEHY (1964).<sup>b</sup>SCHMITT, et al. (1963).<sup>c</sup>FREY, HASKIN, AND POETZ (1965).

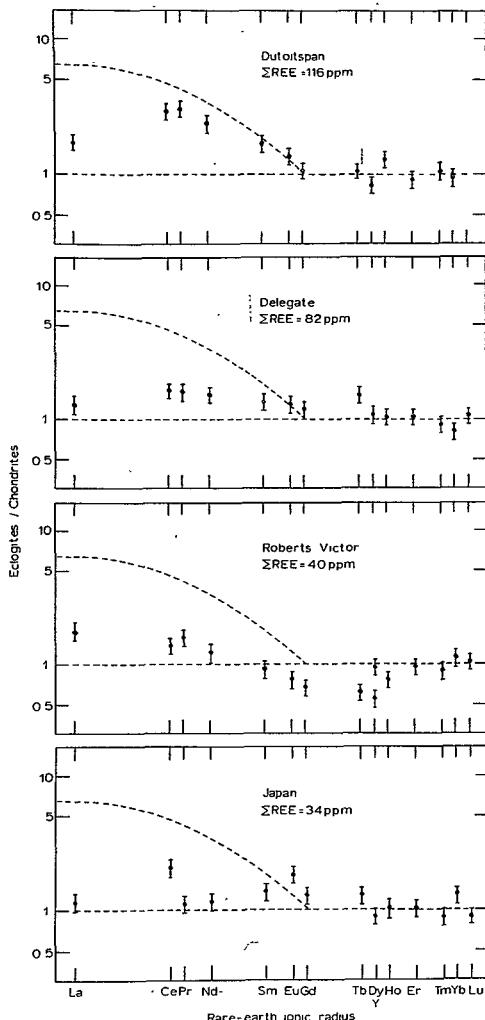


Fig. 17. Comparison plot for eclogites (Table 18).

nearly 1000 ppm and with a RE pattern strongly dominated by the light lanthanides, so even slight contamination by its host material would seriously affect its apparent RE distribution.

The general trend of the patterns of the Dutoitspan specimens is similar to that found for the continental and oceanic island basalts. This is consistent with their potential derivation by partial melting of the mantle, but without the further fractionation during ascent that has been postulated for basalts (O'HARA, 1965).

#### Intermediate Rocks and Granites

Information on RE patterns and concentrations for rocks of intermediate composition is meager. The available analyses are included in Tables 16, 19, and 20. RE patterns for two of the samples, the tonalite and the granodiorite from the southern California batholith (TOWELL, WINCHESTER, and SPIRN, 1965), are shown in Fig. 18. These rocks are intermediate both in absolute RE content and in the extent of relative enrichment in the lighter lanthanides, in contrast to the gabbro and granite from the same batholith which were analyzed. The possible evolution of these patterns through magmatic fractionation is considered in a later section. The Gough Island trachyandesite (Table 16) is another example of a rock of intermediate composition. It has a RE pattern similar to that of the crustal average. The composite of 85 "granites" with <60 per cent  $\text{SiO}_2$  (Fig. 19, Table 19) is certainly made up of rocks of intermediate composition, as are some of the specimens included in the composite of 191 "granites" with 60-70 per cent  $\text{SiO}_2$ . The patterns of these composite samples are very similar to those of the composite of 213 granites with >70 per cent  $\text{SiO}_2$  and the composite of Finnish granites (Fig. 20). The patterns of all the composites closely resemble that of the crustal average. However, La appears to be anomalously enriched in all of them, and Eu is somewhat enriched relative to Gd and Sm in the composite of lowest  $\text{SiO}_2$  content, but depleted in the Finnish and the >70 per cent  $\text{SiO}_2$  composites.

Table 19: REE Contents of Granites (ppm)

	Composite, <sup>a</sup> <60 percent SiO <sub>2</sub>	Composite, <sup>a</sup> 60-70 percent SiO <sub>2</sub>	Composite, <sup>a</sup> >70 percent SiO <sub>2</sub>	Composite, <sup>a</sup> Finnish	USSR <sup>b</sup> (Syenodiorite)	Armenia <sup>b</sup> (Trachyte)	Finnish Archaean <sup>c</sup>	Finnish Granite-Gneiss <sup>c</sup>	Kirovograd <sup>d</sup>
La	68	84	55	47	45	49	43	19	91
Ce	---	---	57	77	110	1100	72	30	170
Pr	9.8	---	7.2	13	16	170	11	7.7	17
Nd	39	55	33	64	64	760	31	24	68
Sm	5.3	8.5	7.1	6.1	14	180	6.0	6.0	12.5
Eu	2.6	1.7	1.12	1.00	---	---	<0.9	2.6	---
Gd	7.9	6.7	7.1	5.7	17	130	13	7.0	7.4
Tb	1.48	1.02	1.25	1.6	---	---	---	2.6	0.17
Dy	---	---	---	---	13	150	3.5	4.3	1.9
Ho	1.39	2.2	1.24	1.13	---	---	---	---	0.26
Er	3.4	3.8	4.4	3.0	11	61	2.6	3.5	0.69
Tm	0.52	---	0.68	0.57	---	---	---	---	---
Yb	3.0	4.0	4.0	3.0	---	---	1.8	2.6	0.23
Lu	0.45	---	---	---	---	---	---	---	0.04
Y	30	44	41	36	---	---	9.5	14	2.5
ΣREE	250	320	220	260	---	2630	200	120	370

Table 19 (continued)

	E. Tuva Nizh-Kad <sup>b</sup>	E. Tuva Radyros <sup>b</sup>	E. Tuva Agash <sup>b</sup>	Ukraine Rapakivi <sup>b</sup>	G-1 <sup>e</sup>	G-1 <sup>f</sup>	Wisconsin Red <sup>g</sup>	Wisconsin Ruby <sup>g</sup>
La	53	130	22	90	.92	102	31	36
Ce	100	210	45	190	150	134	----	----
Pr	12	19	8.7	23	12.9	21	9.7	9.8
Nd	48	58	36	95	55	55	31	43
Sm	11	9.3	9.0	18	8.3	8.6	6.7	8.7
Eu	---	---	---	---	1.36	1.04	0.50	0.69
Gd	11	6.4	9.7	12	----	4.9	5.3	7.0
Tb	4.3	---	---	---	0.64	0.50	0.78	1.34
Dy	12.	4.6	7.9	6.7	2.5	----	----	----
Ho	3.0	---	1.1	---	0.41	0.50	0.91	1.43
Er	8.8	2.3	5.4	3.4	----	1.40	2.7	----
Tm	---	---	---	---	0.16	0.20	----	0.52
Yb	10	1.7	5.5	3.2	0.94	0.63	2.3	4.3
Lu	---	---	---	---	0.12	0.17	0.46	0.77
Y	88	29	72	36	13.3	12.5	21	37
$\Sigma$ REE	370	480	230	310	340	350	180	220

<sup>a</sup>HASKIN, et al. (1965a).<sup>b</sup>BALASHOV (1963a).<sup>c</sup>SAHAMÄ (1945).<sup>d</sup>GAVRILOVA and TURANSKAYA (1958).<sup>e</sup>TOWELL, WINCHESTER, and SPIRN (1965).<sup>?</sup><sup>f</sup>HASKIN and GEHL (1963a).<sup>g</sup>GEHL (1964).

Table 20. REE in Differentiated Intrusive Complexes (ppm)

	Kzyl-Ompul Massif <sup>a</sup>			Susamyr Batholith <sup>a</sup>					South California Batholith <sup>b</sup>			
	Phase 1	Phase 2	Phase 3	Phase 1	Phase 2	Phase 3	Aplites	Batholith Average	San Marcos Gabbro	Bonsall Tonalite	Woodson Mt. Granodiorite	Rubidoux Mt. Leucogranite
La	47	41	80	45	92	63	10	.87	4.0	13.4	25	25
Ce	94	88	120	90	170	120	22	160	14.5	23	34	88
Pr	12	13	12	13	20	14	--	19	2.2	5.7	7.0	5.6
Nd	45	52	33	47	66	53	20	64	7.7	17	22	24
Sm	10	13	3.3	12	11	13	10	11	2.2	3.7	4.0	3.8
Eu	--	--	--	--	--	--	--	--	1.05	1.06	0.80	0.63
Gd	7.7	11	2.6	11	7	12	13	7.8	--	--	--	--
Tb	--	--	--	3.1	--	3.2	--	--	0.48	0.84	0.83	0.63
Dy	8.5	9	1.6	11	6.7	11	22	7.3	2.8	2.6	3.0	3.1
Ho	--	--	--	3.8	--	4.2	--	--	0.57	0.75	0.90	0.74
Er	4.0	5.2	1.0	5.7	3.4	7.4	15	4.0	--	--	--	--
Tm	--	--	--	--	--	--	--	--	0.25	0.39	0.37	0.26
Yb	3.6	5.1	1.0	6.5	3.2	7.4	17	3.8	1.7	2.0	2.9	1.30
Lu	--	--	--	--	--	--	--	--	0.26	0.30	0.39	0.20
Y	40	50	10	64	36	75	150	42	16	22	25	17
ΣREE	280	300	260	330	420	380	290	410	59	97	121	180

<sup>a</sup>BALASHOV (1963c).<sup>b</sup>TOWELL, WINCHESTER, and SPIRN (1965).

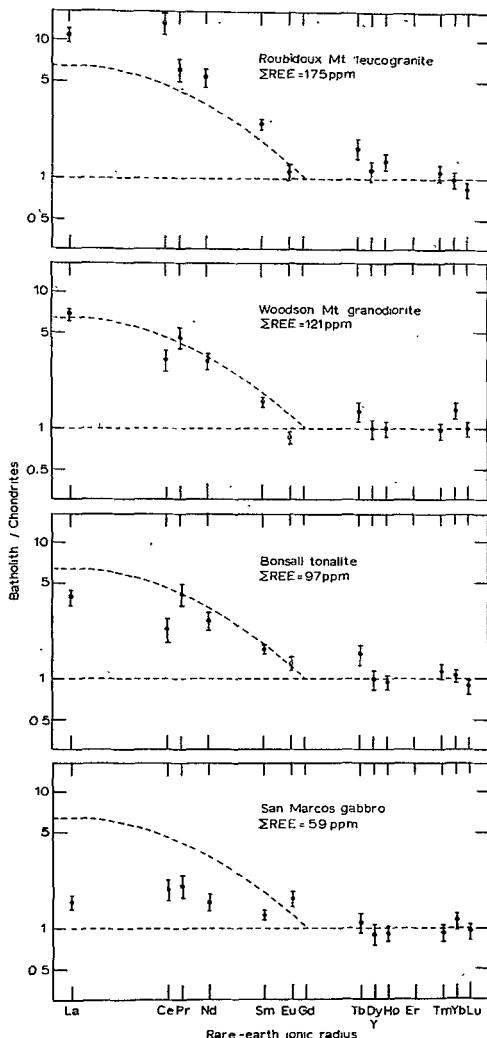


Fig. 18. Comparison plot for phases of the Southern California batholith (Table 20).

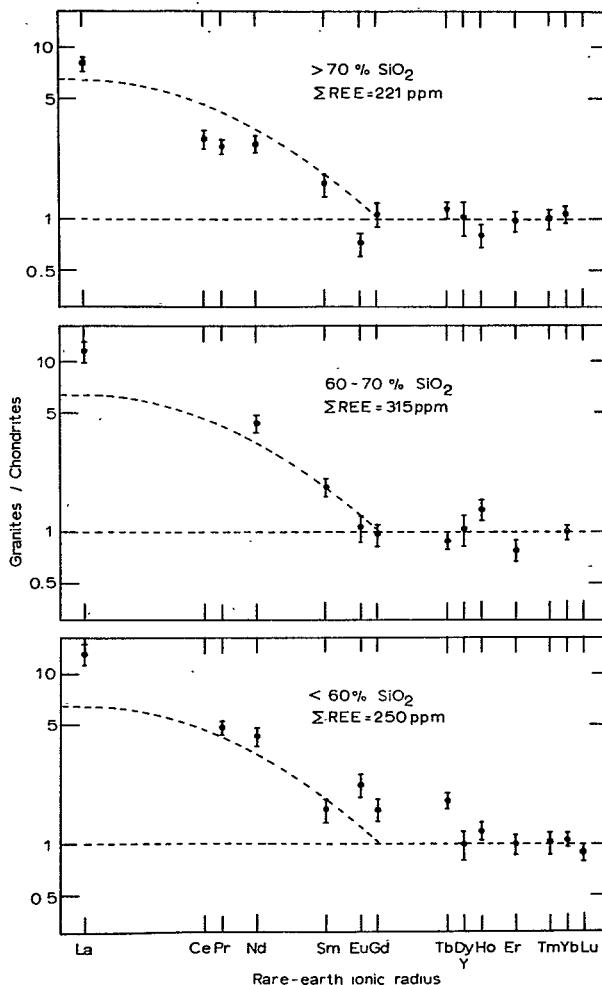


Fig. 19. Comparison plot for 85 "granites" with <60 per cent  $\text{SiO}_2$ , 191 granites with 60-70 per cent  $\text{SiO}_2$ , and 221 granites with >70 per cent  $\text{SiO}_2$  (Table 19).

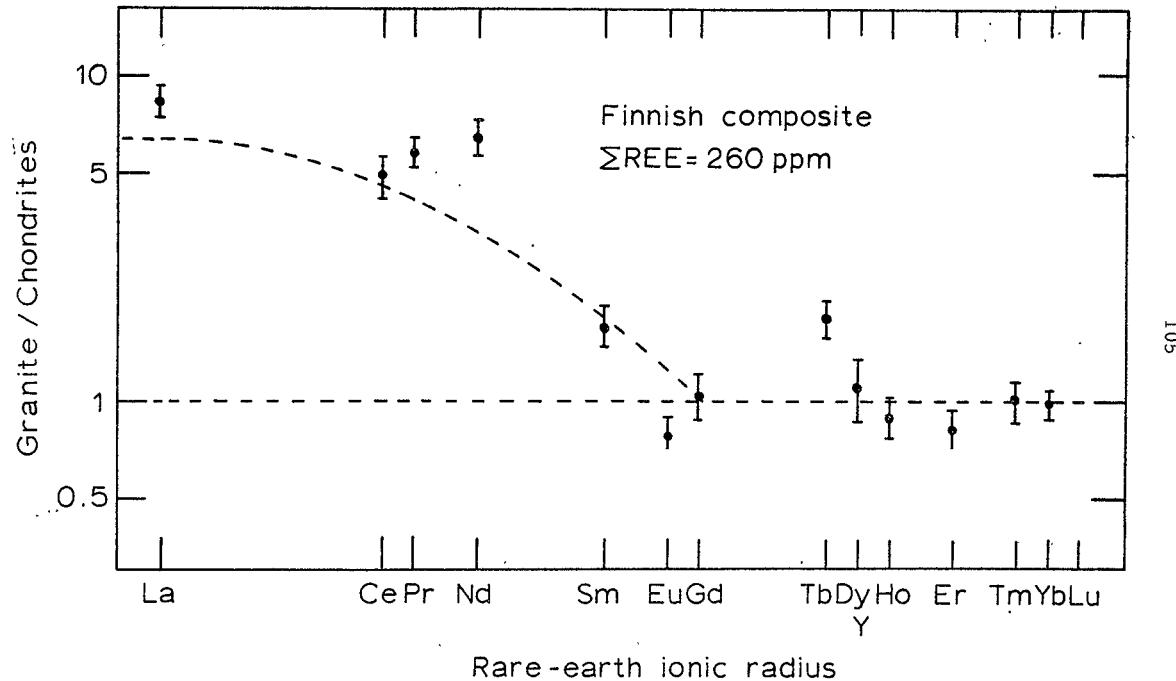


Fig. 20. Comparison plot for composite of Finnish granites (Table 19).

These composite samples provide the best estimate at present of the average RE content and distribution for acid crustal material. It is intriguing that the La excess and Eu deficiency of the granites qualitatively complement the La deficiency and Eu excess of the composite basalt, which results in the average pattern for sedimentary rocks. This will be discussed further in a later section.

The distribution patterns and RE contents of several individual granites are given in Tables 19 and 21 and in Figs. 21-24. A number of these were determined by x-ray spectrography before many of the modern aspects of that technique were developed (SAHAMA, 1945; SAHAMA and VÄHÄTALO, 1941). Nevertheless, the reported values appear to be reasonably accurate, as judged by the smoothness of their comparison curves, and the trends of the patterns are clear. Unfortunately, only relative, rather than absolute, values were obtained for most of these rocks. Several granite analyses were reported by BALASHOV (1963a), but no descriptions of the rocks are included. Two slightly different granites from the same quarry were analyzed by GEHL (1964); their RE patterns were nearly the same. The granite from the southern California batholith, included in Table 20 and Fig. 18, is discussed relative to the other materials from the batholith which were analyzed (TOWELL, WINCHESTER, and SPIRN, 1965) in a following section. The standard granite G-1 was analyzed by two sets of investigators, and the results are in good quantitative agreement, as may be seen from Table 19. FLEISCHER (1965b) mentions some recent granite RE analyses by MELIKSETYAN (1963). The RE patterns of these granites resemble those of G-1 and the Kirovograd granite.

Representative examples of individual granite RE patterns are shown in Figs. 21-24. These range from less relative enrichment in the light REE than the crustal average to the remarkably fractionated distributions of the G-1 and Kirovograd granites. The Finnish Maarianvaara pegmatitic granite has a RE distribution very similar to that of chondritic meteorites.

Table 2: Relative RE : Contents of Some Finnish Granites<sup>a</sup>

	Juva	Ounas	Ubbnäs	Nattinen	Unonen	Astens-Holm	Märtianvaara	Sappi (Granophyre)	Sorkka (Granophyre)	Walamite 17	Walamite 6499	Walamite 6489
La	510	34	260	26	34	26	8.5	17	34	14	77	77
Ce	690	86	430	77	60	43	17	60	77	34	140	130
Pr	170	17	60	17	13	8.6	4.3	8.6	17	6	26	26
Nd	260	68	170	43	43	26	8.6	26	43	17	85	68
Sm	86	17	52	8.6	15	8.6	4.8	8.6	8.6	7.8	26	17
Eu	17	2.6	8.6	1.7	2.6	1.7	0.9	0.9	1.7	0.9	5.2	1.7
Gd	100	17	69	8.7	17	5.7	6.5	8.7	17	7.8	26	26
Tb	17	3.5	8.7	1.7	2.6	1.7	1.7	0.9	1.7	1.7	3.5	2.6
Dy	52	13	26	4.4	13	5.2	8.2	6	8.7	5.2	8.7	17
Ho	17	3.5	8.7	1.7	2.6	1.7	1.7	1.7	2.6	1.7	4.4	2.6
Er	44	8.8	26	2.6	8.8	8.8	6.5	3.5	6.2	3.5	7.0	8.8
Tm	---	1.8	<8.8	<1.7	0.9	0.9	0.9	0.9	0.9	0.9	0.9	1.7
Yb	44	8.8	18	2.6	6.1	3.5	5.3	4.4	5.3	4.4	6.1	8.8
Lu	17	3.5	8.8	1.7	2.6	1.7	1.7	1.8	1.8	1.7	3.5	2.6
Y	240	63	160	24	38	24	19	100	63	24	55	79

<sup>a</sup>SAHAMA and VÄHÄTÄLÖ (1941).

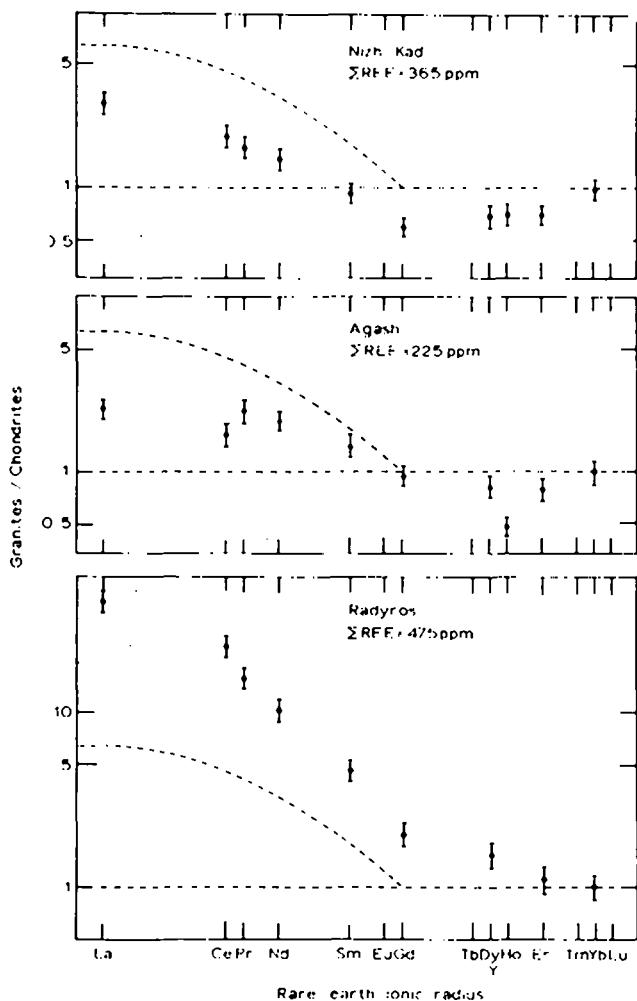


Fig. 21. Comparison plot for some Russian granites (Table 19). Upper dashed curve represents the North American composite shale.

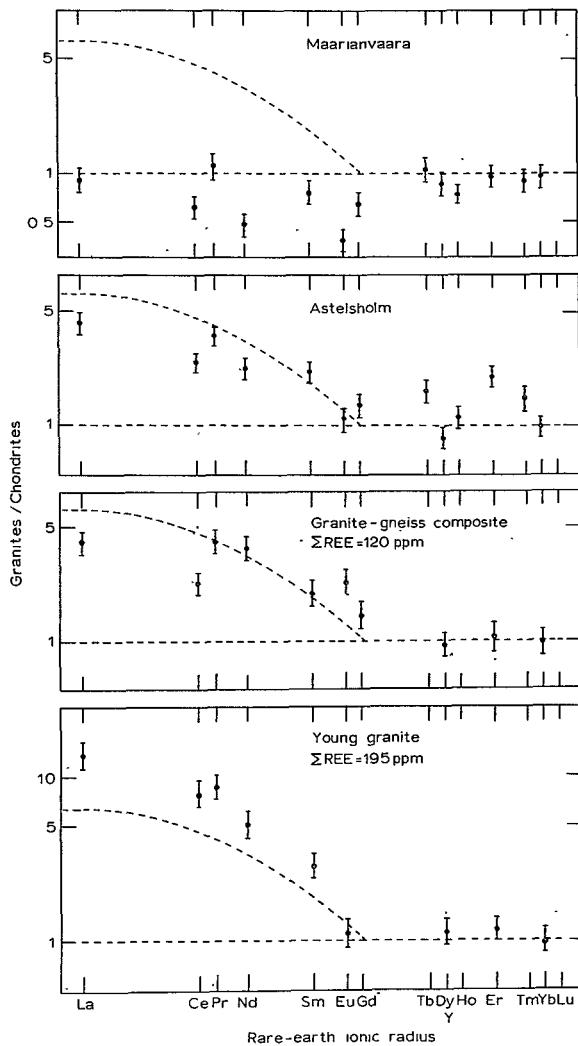


Fig. 22. Comparison plot for some Finnish granites (Table 21).

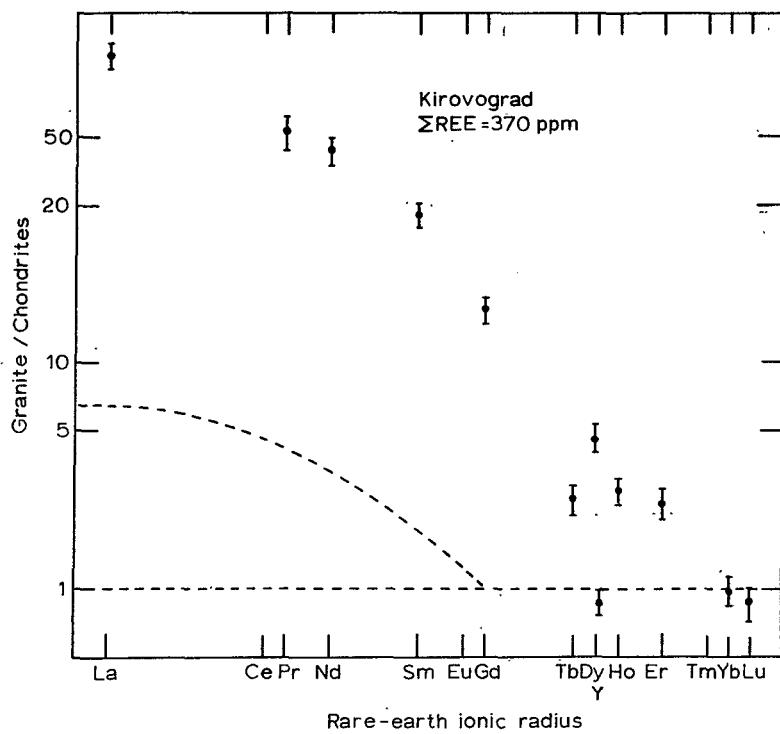


Fig. 23. Comparison plot for Kirovograd granite (Table 19).

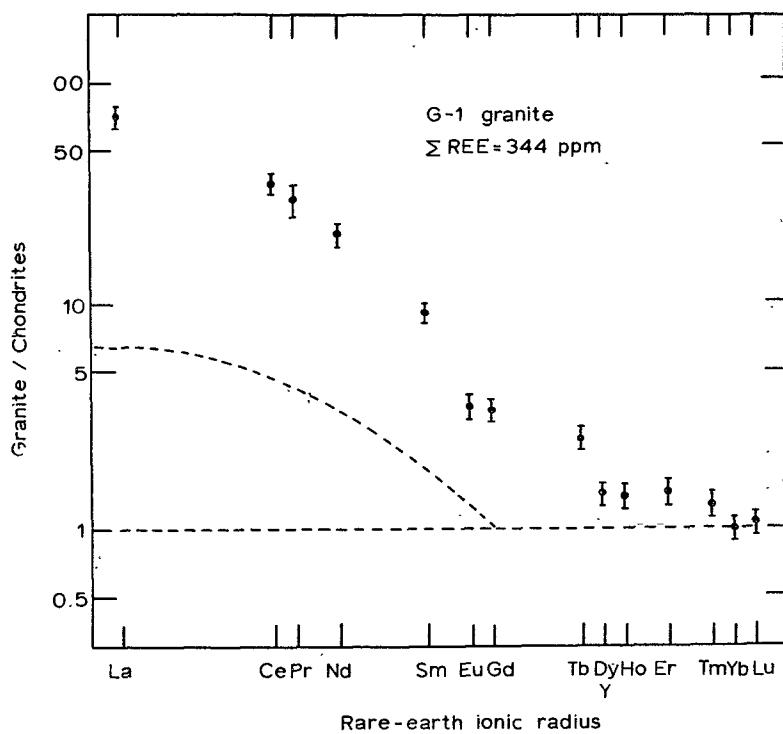


Fig. 24. Comparison plot for G-1 granite (Table 19).

In view of the complexities which would be associated with the formation of pegmatitic material from matter of chondritic composition, the similarity between the RE patterns of the Maarianvaara granite and the chondrites must be regarded as fortuitous, rather than an indication of any close genetic relationship. Several of the granites show relative Eu deficiencies.

"Granites," as generally used and as applied to the samples described above, is an indefinite term which implies little beyond approximate gross composition and texture. The fraction of those substances classified as granites which have magmatic as opposed to metasomatic origins is not a point of agreement among geologists (e. g., TURNER and VERHOOGEN, 1960; WALTON, 1960). Nor is it certain which modes of origin might be best defended on geologic or petrologic grounds for the particular granites whose RE patterns are known. It is to be hoped that once the factors which influence RE patterns are better known and understood, systematic studies of RE distributions in acid rocks will contribute to the solution of the "granite problem." On the basis of the present data, it is probably safe to state that RE contents and patterns like those of the Kirovograd and G-1 granites require for their production an actual melt with considerable amounts of fractional crystallization. Patterns rich in the heaviest REE probably reflect the effects of movement of these elements as soluble aqueous complexes, and would be associated with metasomatism. Such a process might be responsible for the nearly chondrite-like pattern of the Maarianvaara pegmatitic granite.

RE abundances have been determined for three obsidians (Table 22, Fig. 25). Their RE contents and patterns are similar to those of some of the granites.

#### Nepheline Syenites and Alkalic Massifs

More systematic studies have been made for nepheline syenites than for other acid rocks, principally because of the emphasis of several Russian geochemists on studies of magmatic differentiation of the REE in

Table 22. .. RE Contents of Obsidians (ppm)<sup>a</sup>

	Rotorua N. Z.	Ascension Island	Easter Island
La	.28	63	60
Ce	42	----	---
Pr	6. 7	13. 5	34
Nd	----	----	80
Sm	5. 4	14. 1	29
Eu	0. 96	4. 8	7. 6
Gd	4. 5	9. 2	31
Tb	1. 08	1. 40	5. 4
Dy	----	----	---
Ho	1. 07	1. 7	7. 1
Er	3. 2	4. 5	20 —
Tm	0. 53	0. 89	3. 1
Yb	3. 7	5. 0	15
Lu	----	----	2. 6
Y	31	52	160
$\Sigma$ REE	160	350	710

<sup>a</sup>FREY, HASKIN, and POETZ, (1965).

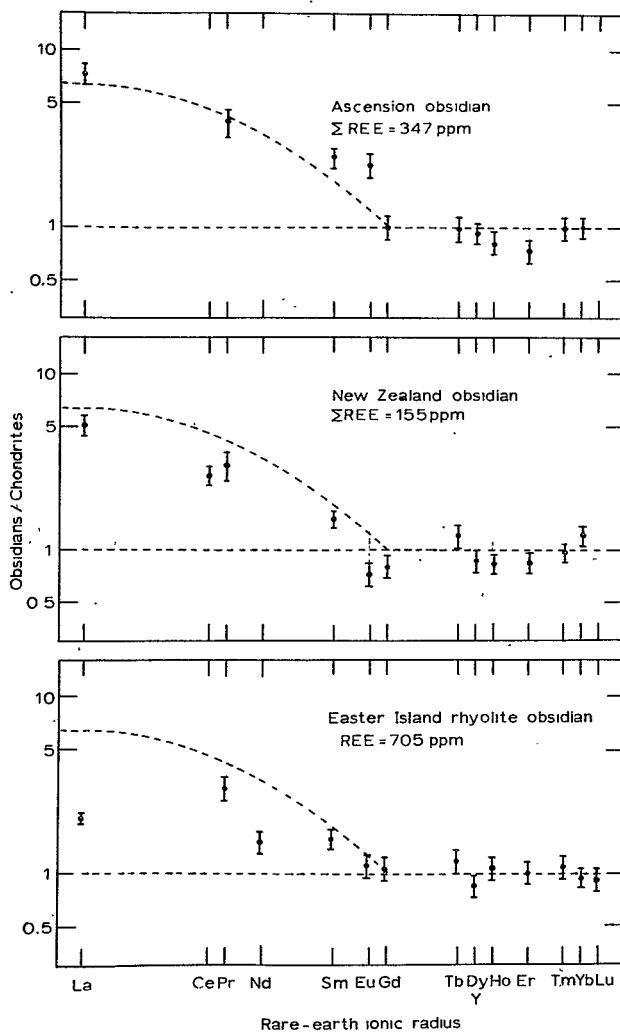


Fig. 25. Comparison plot for obsidians (Table 22).

alkaline massifs. Some nepheline syenites appear to be metasomatic, rather than magmatic, in origin. The results of RE analyses on three such rocks are given in Table 23 and Fig. 26. There is considerable uncertainty about their origins, however. For example, HEWITT (1960) points out that although the nepheline syenites of the Haliburton-Bancroft area have gneissic texture and metamorphic structure, they were emplaced prior to the Grenville orogeny, so the possibility exists that they might have been igneous formations whose features were modified after intrusion. Nothing in their RE contents or patterns appears to favor one type of origin over the other.

The bulk of the RE studies of igneous massifs by the Russian investigators has been summarized by BALASHOV (1963c). He points out that the large variations in RE content and patterns observed among alkaline rocks, granites, and syenites should make these massifs very favorable cases for finding trends in RE pattern evolution during magmatic differentiation. Balashov separates the intrusions of alkaline rocks into three categories, according to whether their alkali contents ( $\text{Na} + \text{K}$ ) considerably exceed, are about the same as, or are lower than their Al contents.

The two largest alkaline massifs considered are the Lovozer-sk (Kola peninsula) and the Illimaussak (South Greenland). Both have  $(\text{Na} + \text{K}) > \text{Al}$ , and are multiphase, well-differentiated intrusions, predominately of nepheline syenites. The formation of the Lovozer-sk massif is believed to have occurred in four phases. The main phases (1-3) are successions of nepheline syenites, and the last phase (4) consists of dikes of alkaline lamprophyres. The average RE contents of the principal phases are given in Table 23. The distribution patterns are displayed in Fig. 27, where the massif average is represented by the solid curve. In gross composition, the later phases of the massif contain higher proportions of mafic minerals than does phase 1. This results in an increase in the extent to which  $(\text{Na} + \text{K})$  exceeds Al in content. Accompanying this trend of increase in

Table 23. RE Contents of Alkali Syenites (ppm)

	Metasomatic (?) Nepheline Syenites			Lovozer-sk <sup>b</sup>			
	Wausau, Wisconsin <sup>a</sup>	Bancroft, Ontario <sup>a</sup>	Red Hill, N. H. <sup>a</sup>	Phase 1	Phase 2	Phase 3	Massif Avg.
La	11.4	29	20	230	380	290	360
Ce	---	----	----	390	690	600	670
Pr	2.6	5.8	5.2	50	73	79	74
Nd	6.8	18	19	180	260	330	270
Sm	1.7	3.0	2.7	37	39	92	48
Eu	0.26	0.40	0.88	----	10	13	10
Gd	1.6	2.7	2.7	24	34	79	42
Tb	0.35	0.43	0.48	5.5	6.5	22	9.3
Dy	---	----	----	14	29	90	40
Ho	0.41	0.46	0.46	3.7	5.0	26	8.8
Er	1.30	1.5	1.8	7.4	15	48	.21
Tm	0.21	0.26	0.27	----	2.7	8	3.5
Yb	1.6	1.49	1.5	5.5	12	46	18
Lu	0.32	0.27	0.27	----	2.0	10	3.4
Y	10.6	13.4	14.2	76	150	480	210
$\Sigma$ REE	60	135	110	1020	1710	2150	1800

Table 23 (continued)

	SANDYK <sup>b</sup>			KHIBINSK <sup>b</sup> , <sup>c</sup>	
	Phase 1	Phase 2	Massif Avg.	Khibinite 5127	Ritschorrite 611
La	40	83	49	1.2	1.4
Ce	75	160	93	2.2	2.4
Pr	9.5	17	11	0.27	0.26
Nd	38	67	44	1.00	1.00
Sm	8	12	9	0.16	0.16
Eu	---	---	---	---	---
Gd	6.5	7.5	7	0.12	0.16
Tb	---	---	---	0.03	0.05
Dy	4.5	5.0	4.8	0.10	0.22
Ho	---	---	---	0.03	0.05
Er	3.0	3.0	3.0	0.04	0.11
Tm	---	---	---	---	---
Yb	(3.0)	(3.0)	3.0	0.5	---
Lu	---	---	---	---	---
Y	30	33	31	0.6	1.1
$\Sigma$ REE	220	400	260	480	200

<sup>a</sup>HASKIN, et al. (1965a).<sup>b</sup>BALASHOV (1963c).<sup>c</sup>Values normalized to Nd.

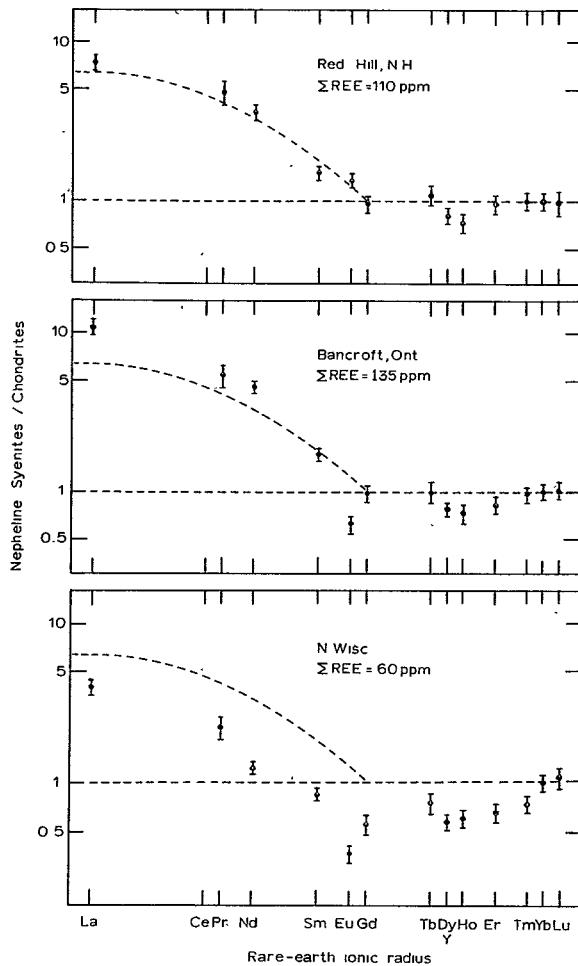


Fig. 26. Comparison plot for nepheline syenites (Table 23). Upper dashed curve represents the North American composite shale.

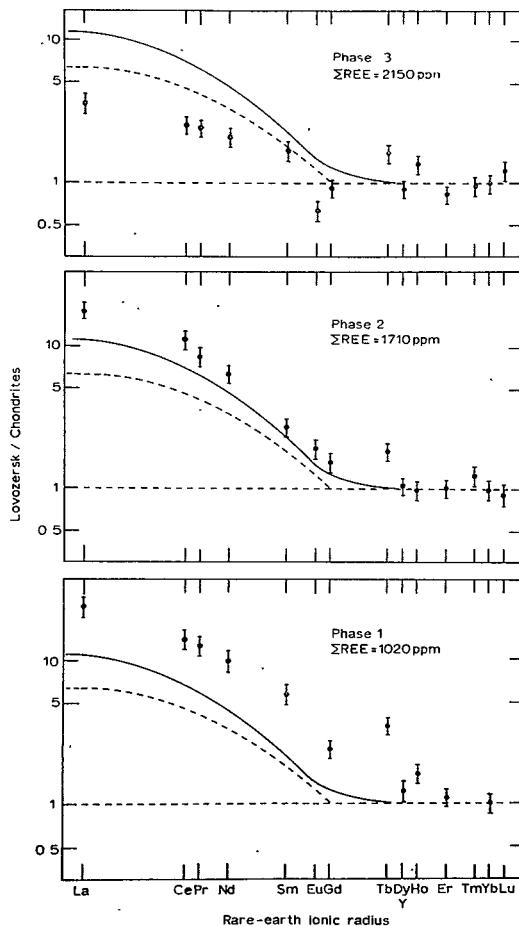


Fig. 27. Comparison plot for phases of the Lovozeresk massif (Table 23). Upper dashed curve represents the North American composite shale. Solid curve represents massif average.

mafic minerals is an increase in total RE content, and in the proportion of heavy lanthanides and Y in the distribution pattern. On the whole, the Lovozersk massif is several times richer than average crustal material in RE content, and is relatively more enriched in the light lanthanides.

The differentiation and mineralogy of the Illimaussak batholith are very similar to those of the Lovozersk massif. Fewer analyses were available for the Illimaussak, but it was concluded that the evolution of the RE patterns was much like that in the Lovozersk for the alkaline phases. However, the earliest phase (gabbroid and syenitic rocks) was found to be relatively richer in the heavier lanthanides and Y than the immediately succeeding alkaline rocks. This suggested that the REE were accumulated from gabbroids into the earliest syenites, with enrichment of the heavy REE from the latter to the more mafic, still later phase.

Examples of alkaline intrusions with less (Na + K) than Al for which RE data were available are the Sandyk (central T'ien-Shan) and Vishnevyye Mountains. (Ural area) massifs. These intrusions exhibit less structural and compositional variation than the massifs described previously.

The Sandyk massif consists of two phases, the first composed of alkaline gabbroids and alkaline-earth syenites and the second of alkaline and nephelinic syenites. On the average, the potash content was about twice that of soda in these rocks. In contrast to the previous examples, the proportion of mafic minerals is less in the later differentiates than in the earlier phase. The RE contents of the two phases are given in Table 23 and the distribution patterns are shown in Fig. 28. The rocks of phase 1 are seen to have essentially the same RE content and distribution as the average for the earth's crust. Phase 2 is considerably enriched over phase 1 in RE content, and has a considerably higher proportion of light lanthanides in its distribution pattern.

The REE pattern of the Vishnevyye syenites shows an even higher proportion of light lanthanides than does phase 2 of the Sandyk massif. Both massifs are characterized by a relative enrichment of the lighter lanthanides in their late differentiates.

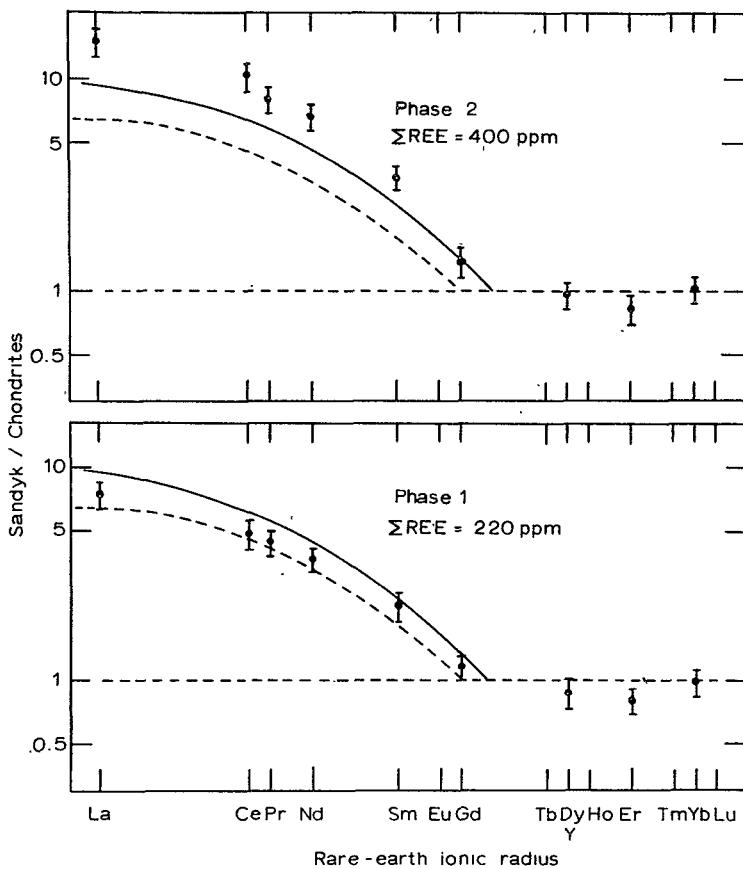


Fig. 28. Comparison plot for phases of the Sandyk massif (Table 23).  
Solid curve represents massif average.

The Khibinsk massif (Kola peninsula) is a multiphase intrusion of nepheline syenites in which  $(K + Na) \sim Al$ , and in which  $Na > K$ . Most of the phases have RE patterns similar to that of khibinite No. 5127 (Table 23, Fig. 29). The khibinite has two to three times the average RE content of the earth's crust, and a relatively higher proportion of the lighter lanthanides. Only one phase (ritschorrites) was appreciably different in RE content and pattern from the rest, and it is uncertain whether that phase has a magmatic or metasomatic origin.

From the studies of these massifs, Balashov drew the following conclusions regarding the behavior of the REE:

1. RE differentiation among magmatic phases was observed for all the alkaline massifs, and the ranges in compositional variation were similar for the various massifs.
2. The RE patterns of those phases containing relatively low proportions of mafic minerals tended to be relatively richer in the lighter lanthanides than the patterns of phases with high proportions of mafic minerals.
3. All the massifs contained a relatively higher proportion of the light REE than does the earth's crust.
4. The absolute RE contents of the massifs ranged from about twice to nearly ten times the crustal average. The highest RE contents accompanied the excess of  $(Na + K)$  over  $Al$ .
5. The massifs with  $(Na + K) > Al$  tended to concentrate the light REE toward the end of magmatic differentiation, while the opposite was true for those with  $(Na + K) < Al$ .

Thus, Balashov concludes that the nature of the alkaline magma substantially influences RE behavior during the magmatic differentiation...

PAYLENKO, VAINSHTEIN, and TURANSKAYA (1959) made an extensive study of RE minerals and RE concentrating minerals in the igneous complexes of eastern Tuva. On the basis of their studies of these minerals, they concluded that the RE patterns in the RE concentrating minerals are

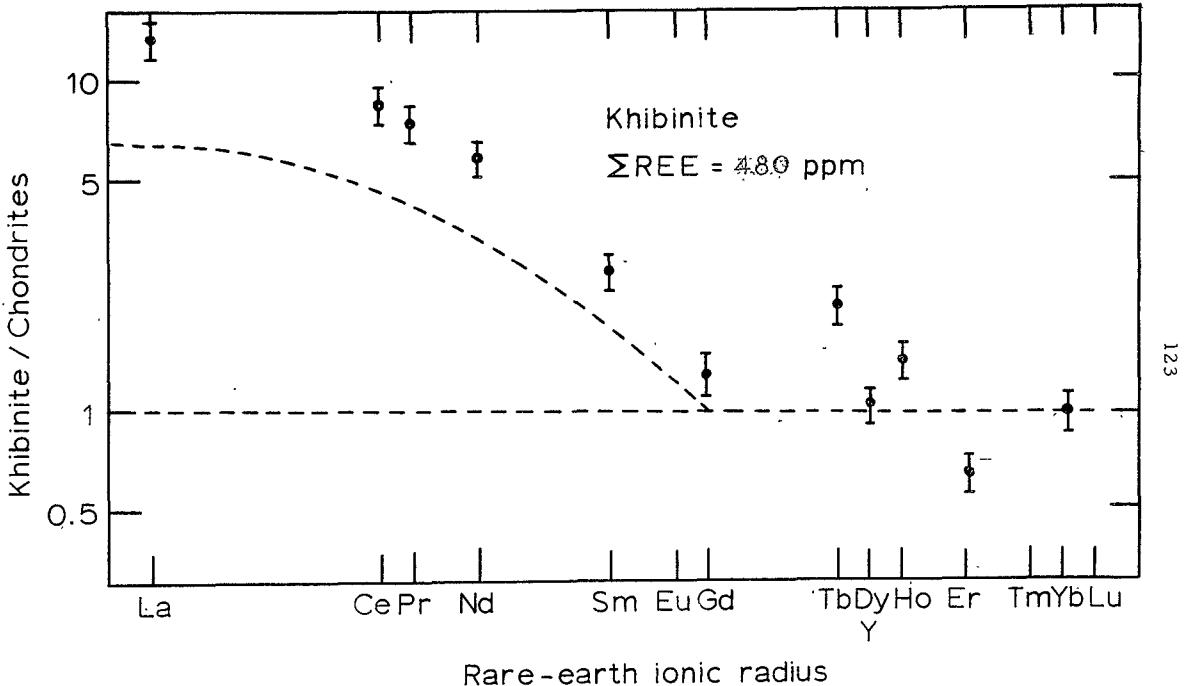


Fig. 29. Comparison plot for khibinite (Table 23).

determined primarily by the RE pattern of the magma from which the minerals derive and by the relative mobilities of the various members of the RE group.. The crystallochemical character of the capturing minerals was felt to be of less importance. Variations in both absolute RE content and relative RE abundances were found with both the age and alkalinity of the rocks. These authors believed that the crystallochemical character of the minerals did affect the RE patterns significantly when several light-lanthanide favoring minerals were being formed simultaneously. In such cases, the mineral offering the highest coordination number for the REE showed the greatest Ce/Nd ratio.

It was also concluded that the final magmatic products of some regions appeared to be relatively enriched in the heavy lanthanides and Y. Differences in the behaviors of Y and the heavy lanthanides during metasomatic processes were noted. For example, the Y/heavy lanthanide ratio was lower in fergusonites from rocks of metasomatic origin than in those from granite pegmatites.

Highly alkalic complexes containing nepheline syenites were found to be richer in light REE than in heavy REE, regardless of their ages.

The processes of mineral formation were thought to concentrate Y and the heavy lanthanides in pegmatites and marginal parts of metasomatic zones, but with increasing intensity of metasomatism there was a shift favoring the light lanthanides. Potash metasomatism appeared to effect a more complete removal of the REE from rocks than soda metasomatism. The heavy lanthanides appeared to be more mobile than the light REE, and Pavlenko, Vainshtein, and Turanskaya postulated that this might be explained by the relatively greater solubilities of alkali carbonate complexes of the heavy lanthanides as compared with those of the lighter members of the series. Y was found to be more mobile than any of the lanthanides, a fact which was curiously attributed to its lower atomic weight.

As a result of a further study of the rocks of eastern Tuva (VAINSHTEIN, et al., 1961), based on RE analyses of whole rocks as

opposed to concentrating minerals, the conclusions of the previous (above) work were modified in some measure. Only Ce/Nd ratios were used, however. A more systematic selection of material from among the granites, syenites, and nepheline syenites of the complex was made, and greater care was taken to establish spatial and genetic relationships among the rocks.

No definite relation could be found between relative RE content and acidity, basicity, or content of any major rock components, including the alkalis. The range of variation of Ce/Nd in granites and syenites (1.25-3.7) was not distinct from that of the nepheline syenites (1.35-4.9). It was noticed that for granitoids and nepheline syenites the Ce/Nd ratio tended to increase with increasing alkali activity during crystallization.

#### Other Differentiated Magmatic Complexes

As an example of a magmatic chamber of syenitic composition, BALASHOV (1963c) selected the Kzyl-Ompul massif (Kirgiz Range, north T'ien-Shan). This massif consists of three intrusive phases. The oldest phase is of syenitic composition, the intermediate phase is of granosyenitic composition, and the final phase consists of granites with very low mafic mineral contents. In all phases,  $K > Na$ . The RE contents of the phases are given in Table 20 and are shown in Fig. 30. The evolution of the RE patterns resembles that of the Sandyk massif, which was also characterized by  $K > Na$ . It is interesting to note that both the RE content and distribution of the Kzyl-Ompul massif are essentially the same as for the crust.

Balashov also discusses RE differentiation in the Susamyr batholith, which consists of three phases and is granitoid in composition. The oldest phase is represented by bosses and xenoliths of gabbrodiiorite and diorite. The intermediate phase is of granodioritic to granitic composition. The final phase consists of granite of very low mafic mineral content and contains veins of aplite. From the earliest to the latest phase, the alkali content increases, and the Ca, Mg, and Fe contents decrease sharply. The RE

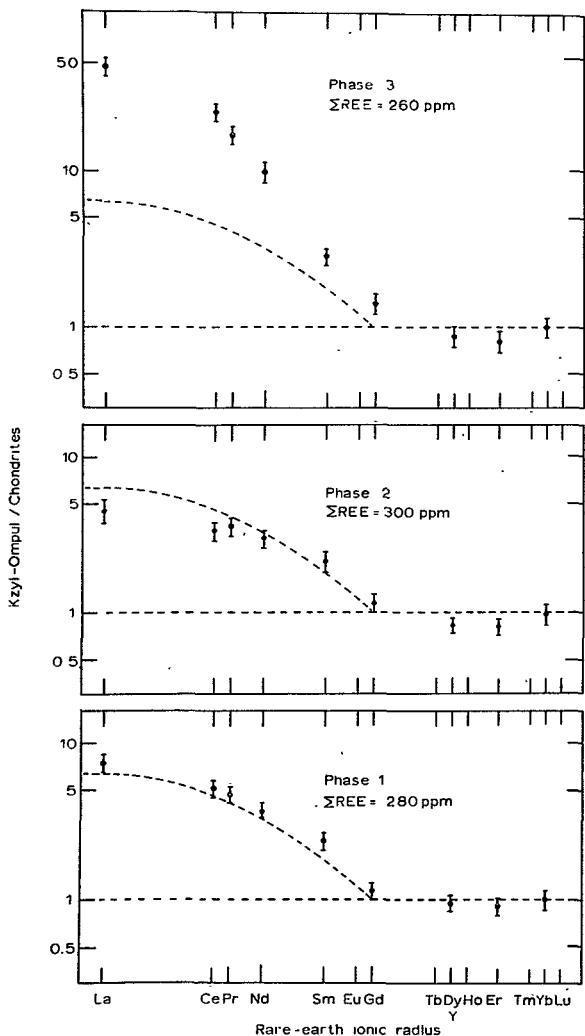


Fig. 30. Comparison plot for phases of the Kzyl-Ompul massif (Table 20).

contents of the phases and of the aplites are given in Table 20 and the patterns are shown in Fig. 31.

The average RE content of the Susamyr batholith is about 1.5 to 2 times the crustal average, and the pattern for the batholith as a whole is significantly enriched in the light REE as compared with the crustal pattern. The evolution of the RE patterns was stated to be complex in nature, with an increase in RE content and extent of predominance of the light REE in phase 2 over phase 1, followed by a decrease in both for phase 3. Finally, the aplites are characterized by RE patterns which are highly enriched in the heavy REE. Balashov notes that the evolution of the RE patterns in the batholith does not follow in any simple way the monotonic increase in rock acidity which characterizes the development of the batholith.

The observed evolutions of the RE patterns in the massifs and batholiths, plus other data, led Balashov to conclude that either the light or the heavy lanthanides can be concentrated toward the end of magmatic differentiation, or in a particular phase of an intrusion.

An interpretation of RE patterns in massifs or batholiths as the direct result of magmatic fractionation must be regarded with some caution. It is not easy to determine the composition of an igneous body of great size, or to know whether such an average composition represents that of the magma which gave rise to the body. Where several phases are present, implying more than one injection of magma, it does not necessarily follow that they represent differentiates of a single, original melt whose composition was unaltered except by physicochemical processes accompanying cooling. It is difficult to evaluate the role of material assimilated by the melt.

Studies of four materials from the southern California batholith were made by TOWELL, WINCHESTER, and SPIRN (1965). The phases examined were a gabbro, a tonalite, a granodiorite, and a granite. The batholith is believed to have resulted from differentiation of gabbroic magma at depth

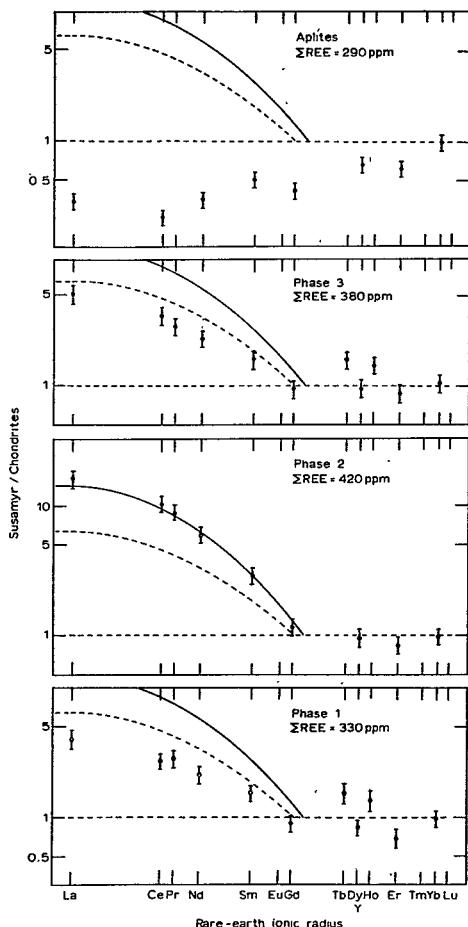


Fig. 31. Comparison plot for phases of the Susamyr batholith (Table 20). Upper dashed curve represents the North American composite shale. Solid curve represents massif average.

(LARSEN, 1948). The results of a study by TAYLOR and EPSTEIN (1962a,b) of oxygen isotope fractionation in these same rocks are in qualitative agreement with that interpretation. However, Taylor and Epstein deem it unlikely that the granite resulted from simple fractional crystallization of the granodiorite magma, but do not exclude the possibility that both the granite and granodiorite might have derived directly from the tonalite magma. The gabbro is known to be somewhat variable in gross compositions. Hence, there remains considerable uncertainty in the history of development of this large and complex plutonic body, as is emphasized by TOWELL, WINCHESTER, and SPURRN (1965 in their interpretations).

The results of the determinations for the batholith rocks are given in Table 20. The evolution of the RE patterns is shown in Fig. 18, where it is seen that both the total RE content and the preference for light lanthanides increase as the acidity of the rocks increases. This trend is similar to that of the oceanic island suites (FREY, HASKIN, and POETZ, 1965) and to that of the presumed development of the earth's crust from material of ultrabasic composition. It contrasts with the trend found for the somewhat similar Susamyr batholith described above (BALASHOV, 1963c). However, the aplites described by Balashov, in which the heavy lanthanides and Y were predominant, are probably the result of reactions of late solutions. Their RE patterns are those characteristic of complexing in solutions, and so may not be due to effects of magmatic crystallization. Thus, the trend of increasing RE content and preference for the light REE with increasing acidity may be a general characteristic of purely magmatic differentiation. This can be determined only with much further work.

It is of interest to note that the absolute RE content of the southern California batholith is somewhat lower than the average for the earth's crust, and that the RE patterns range from that of the gabbro, in which the light REE are only a little enriched relative to chondrites, to that of the granite, in which the light REE are even more enriched relative to chondrites than they are in average crustal matter.

TOWELL, WINCHESTER, and SPIRN (1965) also showed that Eu suffered a systematic removal relative to the other REE from the more acid rocks during magmatic crystallization. This they regarded to be a consequence of reduction of Eu to the +2 oxidation state. They obtained linear correlations between the extent of Eu depletion and both the acidity of the rock and the oxygen isotope fractionation, as determined on the same materials by TAYLOR and EPSTEIN (1962a, b).

SAHAMÄ and VÄHÄTALO (1941) gave RE values which occur as pipes in the diabases of Sorkka and Säppi, and for similar material (walamites) from diabases near Walamo. These values are listed in Table 21. The RE patterns of these materials are similar to those of the crustal average, except that two are less strongly enriched in the lighter lanthanides. While the RE patterns in the granophyres and walamites were quite similar, there was conflicting opinion among geologists as to whether the granitoid materials were genetically related to the diabases. Thus, Sahama and Vähätalo could conclude only that if the materials were products of the same magmatic crystallization, the resulting RE patterns offered no obvious indication of it.

#### Carbonatites

VAINSHTEIN, POZHARITSKAYA, and TURANSKAYA (1961) performed analyses to determine the REE in carbonatites from the Eastern Sayan Mt. massif, a complex pneumatolytic-hydrothermal body. The massif appears to have been emplaced in at least two clearly distinguishable stages. The early phase of stage 1 consisted of calcite carbonatite with mica, magnetite, and accessory apatite. In the later phases of stage 1, these minerals gave way to a suite of amphibole, pyrrhotite, and pyrochlore. Stage 2 is characterized by ankerite, further apatite, and several other minerals, the important RE concentrators being monazite, parisite, bastnäsite, and fluorite.

In the early phases of stage 1, the REE were entirely dispersed in the calcite and apatite. In the later phases, 85 to 90 per cent of the REE

was still in the calcite and apatite, but they were also concentrated in the pyrochlore, contributing up to 4 per cent of the mass of that mineral. In the ankeritized material of stage 2, the degree of concentration of the REE increased. In the monazite-bearing, ankeritized calcium carbonate, as much as 50 per cent of the total RE content is in monazite. In the parisite-bearing portions, over 90 per cent of the REE is in the parisite, with the remainder dispersed in the ankerite and apatite. The onset of ankeritization was accompanied by a 2- to 3-fold increase in total RE content over the earlier, monazite-free carbonatite, and the total RE content in the final ankerite carbonatite is 7-10 times that of the earliest calcite carbonatite. The RE content of the calcite ranges from 0.10 to 0.16 per cent, averaging 0.14; that of the ankerite ranges from 0.06 to 0.09 per cent, averaging 0.07; and that of the apatite ranges from 0.4 to 0.7 per cent, averaging 0.56.

Vainshtein, Pozharitskaya, and Turanskaya suggested that the fairly constant RE content found for calcites in all generations and in the ankerite indicates that the limit for diadochic substitution was reached. This would also help account for the increase in total RE content with time.

The light REE are predominant in all of the minerals, and both monazite and parisite are strongly selective in favor of the lightest lanthanides. As the RE contents of the carbonatite increased toward the later phases, there was an accompanying increase in the relative amounts of Ce and La. Two calcite analyses from this work are included in Table 24.

Two African carbonatites were analyzed by SCHOFIELD and HASKIN (1964). The total RE contents were found to be much higher than in sedimentary carbonates, as is typical for a number of trace elements in carbonatites (TURNER and VERHOOGEN, 1960). The results of these two whole rock analyses are given in Table 24 and Fig. 32. The patterns are markedly different from those of sedimentary carbonates, which are usually quite close to the average pattern for sedimentary rocks. Such differences might prove useful in distinguishing between sedimentary and igneous origins of carbonates.

Table 24.. RE Contents of Carbonatites and Contained Minerals (ppm)

	Calcite CK-4-20 <sup>a</sup>	Calcite CK-4-12 <sup>a</sup>	Panda Hill, Tanganyika <sup>b</sup>	Sangu Tanganyika <sup>b</sup>	Avg. for Pyrochlores <sup>c</sup>
La	1.2	1.2	180	76	11.6
Ce	2.2	1.9	270	390	56
Pr	0.27	0.24	67	25	6.8
Nd	1.0	1	280	94	21
Sm	0.18	0.18	46	18	2.5
Eu	---	---	14.3	6.7	0.35
Gd	0.16	0.16	34	17	1.06
Tb	0.02	0.02	11	2.5	0.13
Dy	0.09	0.07	---	---	0.33
Ho	0.02	0.015	5.1	2.1	0.1
Er	0.02	0.015	14.5	4.5	0.17
Tm	---	---	4.5	0.53	---
Yb	0.007	0.007	9.0	1.5	0.30
Lu	---	---	2.4	---	---
Y	0.23	0.20	95	38	---
$\Sigma$ REE	---	---	---	---	2200

<sup>a</sup>VAINSHTEIN, TUGARINOV, and TURANSKAYA (1961); values are relative, not absolute.

<sup>b</sup>SCHOFIELD and HASKIN (1964).

<sup>c</sup>BORODIN and BARINSKII (1961); values are relative, as per cent of total REE.

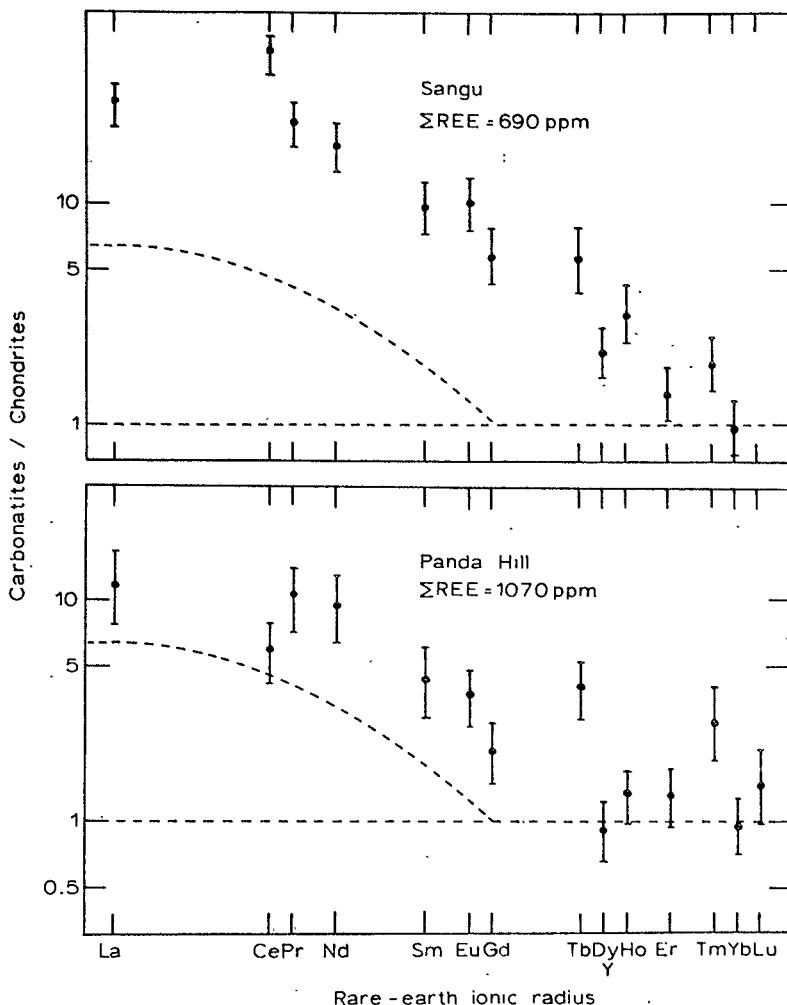


Fig. 32. Comparison plot for carbonatites (Table 24).

The REE were studied in pyrochlore from carbonatites by BORODIN and BARINSKII (1961). RE patterns strongly dominated by the lightest lanthanides were observed.

Metasomatic and Hydrothermal RE Transport:

KOSTERIN (1959) considered the problem of the formation of economically valuable concentrations of REE in hydrothermal deposits. He pointed out that the occurrences and mineral associations in the majority of cases are characterized by the presence of the alkali metals and the anions of weak and intermediate acids, e.g.,  $H_2CO_3$  and HF. The evidence suggests to him that the RE transporting solutions were alkaline and contained  $HCO_3^-$ ,  $CO_3^{=}$ ,  $F^-$ , and, in some cases,  $HSO_4^-$  and  $SO_4^{=}$ . The REE could not be transported as simple ions in such solutions; complexing is necessary for them to be carried for any great distance. As the alkalinity of such solutions of complexes decreased, the complexes would break and the REE would precipitate. Since the heavy REE form more stable complexes than the light REE, Kosterin suggests that they would become relatively enriched in solution and dominate the late-stage deposits. Carbonate complexes are believed to be the most important. These could be broken by sudden expansion of the solution into a cavity with consequent release of pressure on the  $CO_2$ , by lowering of the  $CO_2$  concentration in the solution, by albitization wherein the Na concentration of the solution would be drastically reduced, or by precipitation of insoluble carbonate species by assimilated Mg, Fe, or Ca ions.

BANDURKIN (1961) has discussed the movement of the REE as complex carbonates under hydrothermal conditions. (This possibility was first pointed out by INGERSON (1958) for the bastnäsite deposits of southern California.) Bandurkin concluded that  $CO_2$  transport cannot explain the origins of the RE minerals in high temperature greisen deposits. He called attention instead to a strong genetic relation in these deposits between the REE and F, especially when the REE are associated with deposits of Fe,

Al, Sn, Be, or Zr. He cited evidence that the REE are not quantitatively precipitated in the laboratory by F when certain cations (Al, Fe, Zr, Th, Mn, U, or Be) are also present in the solution. This suggests mixed complex formation. Geologically, it should be possible to combine large amounts of high-valence cations,  $F^-$ , and small amounts of REE to give complexes of the type  $[Me^{III}F_2]^{+} [REF_4]^-$ , etc. The transport of such complexes would occur in acid solution.

An excellent study of RE transport through complexing was made by MINEYEV (1963). He began his discussion with a summary of previous observations, which include the following:

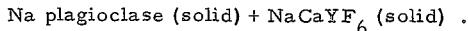
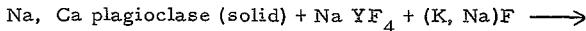
1. Only complexing could emphasize the differences among the properties of the individual REE to allow fractionations as severe as many of those observed in nature. Certainly, migration of these elements as simple ions would be inadequate.
2. High concentrations of the REE, and especially of Y and the heavy lanthanides, are associated with high concentrations of alkalis and volatiles, and are not typical of normal igneous rocks not enriched in alkalis and volatiles.
3. There is experimental evidence for the stability under hydrothermal conditions of complexes of the  $NaYF_4$  type.
4. Paragenetic association of the REE with Al, Be, Fe, Zr, Sn, and other complexing elements, plus  $F^-$ ,  $Cl^-$ ,  $CO_3^{=}$ ,  $PO_4^{=}$ , etc., is proof of their simultaneous presence in mineral-forming solutions. Also, very slightly soluble RE complexes are known to occur as natural minerals.

Mineyev then proposed to show that the geochemical differentiation of the REE is caused by migration of those elements in the form of complexes, coupled with regular variations in the acidity of postmagmatic solutions. He described a study of a series of rocks in a Kazakhstan massif. The massif, presumably originally biotite granite, suffered a sequence of post-magmatic alterations which can be approximately

summarized as microclinization-albitization-silicification-albitization-microclinization, indicating considerable variability in the acidity of the metasomatizing solutions. The bulk of the massif appears to be relatively impoverished in REE, ranging from ~25-90 ppm. Riebeckite-albite, aegirine-albite, and astrophyllite-albite metasomatics near the periphery of the massif were significantly enriched in REE (~850-6500 ppm). RE mineralization was found in the adjacent wall rocks.

Mineyev succeeded in correlating the movement of the REE and the RE patterns in the metasomatites with the fluoride contents of the metasomatizing solutions and their acidities. A regular sequence of evolution of RE patterns had developed from the central to the peripheral parts of the massif, with the lightest REE predominating in the patterns near the center but giving way to Dy maxima, and finally Yb maxima at the outermost edges. There was a corresponding increase in the fluoride and alkali contents of the rocks as the RE patterns shifted to favor the heavier REE. Examples of the RE patterns are given in Fig. 33 and Table 25.

Mineyev reasoned that the observed behavior should be expected if the REE were carried in solution as complex alkali fluorides. As albitization set in, the  $\text{Na}^+$  in the solution would be used up in forming the new mineral complex of the rock. The decrease in  $\text{Na}^+$  content would cause precipitation of insoluble fluorides, including those of the REE. The reaction could be written as follows:



The weakest light REE complexes would break first and would precipitate. The residual solution would be increasingly relatively enriched in the heavy lanthanides and Y. These, too, would precipitate when the alkali content of the solution became too low. Further substantiating evidence is the observation of the mineral gagarinite,  $\text{NaCaYF}_6$ , in the Ca-rich wall rock

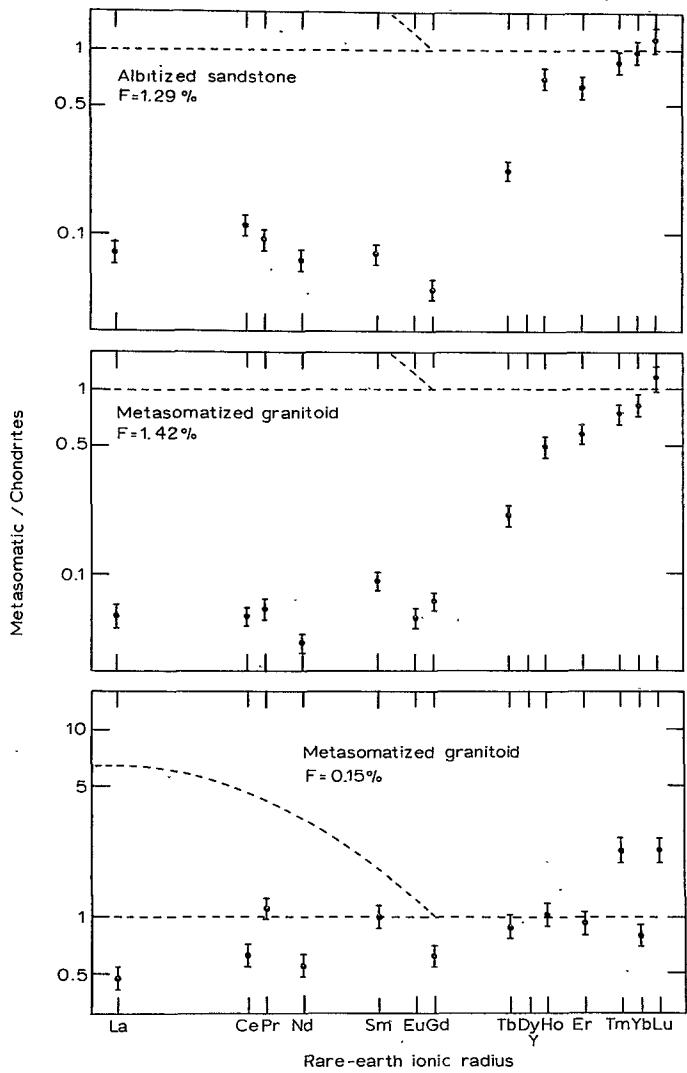


Fig. 33. Comparison plot for metasomatized granitoids (Table 25).

Table 25. Relative RE Contents of Some Metasomatic Specimens<sup>a</sup>

	Metasomatized Granitoids		Albitized Sandstone No. 6	Gagarinite
	No. 1, Low F	No. 4, High F		
La	5.7	3.0	2.7	1.5
Ce	22	8.4	11.1	8.4
Pr	5.5	1.3	1.3	1.5
Nd	12.8	4.0	4.8	3.8
Sm	8.1	3.0	1.8	8.2
Eu	0.3	0.7	-----	0.3
Gd	8.1	1.7	1.3	2.9
Dy	12.8	17.	27	21
Ho	3.1	5.7	5.8	4.4
Er	8.1	20	16	15
Tm	2.9	3.7	3.1	2.4
Yb	5.7	23	20	12.1
Lu	2.9	5.7	4.0	4.4
F	0.15	1.42	1.29	

<sup>a</sup>MINEYEV (1963); REE values are relative, not absolute, but F contents are absolute.

bordering the metasomatites. Mineyev suggested that similar complexing-acidity relationships can explain the behavior of the REE and their mineral sequences in pegmatites.

Certainly, the mechanism proposed by Mineyev offers a plausible method for the production of RE patterns relatively rich in various heavy REE, such as those of Fig. 33. Similar patterns in strictly magmatic acid rocks are not known, and would seem difficult to produce by fractional crystallization of a light-REE dominated silicate melt.

#### Pegmatites

KALITA (1959) has studied the RE minerals in pegmatites of north-western and southwestern Karelia. Most of the pegmatites consist of quartz-plagioclase-microcline zones, with metasomatic zones bordering the pegmatite cores. From the pegmatite border to the core, the following zones are distinguished:

1. Quartz-albite-oligoclase.
2. Coarse grained albite.
3. Muscovite in large sheets.
4. Pods and fracture fillings of saccharoidal albite and greisen muscovite.

There are two distinct groups of RE minerals. The first, mainly light-REE-rich monazite and allanite, is associated with the coarse grained, albite and large sheet muscovite. These minerals were shown to have formed during the initial stages of albitization as a result of direct replacement of microline. The second group includes blomstrandine, pyrochlore, obruchevite, and betafite, all richest in Y, Gd, and Dy. These minerals are related to the activity of late stage solutions, which produced the pods and fracture fillings of zone 4.

The sequence of formation of the minerals was carefully determined, and the RE patterns were studied. It was apparent that the light REE separated from the solutions during the early stages of replacement, and

the heavy lanthanides and Y became concentrated for separation during the later stages. Reactions by late, strongly basic solutions on the heavy-REE-rich minerals produced secondary minerals that were low in these elements. It was also concluded that the RE patterns in the minerals could not be explained strictly on the basis of coordination number in the crystal lattices, but were related to the relative basicities of the REE and their solutions.

ZHIROV, GANDURKIN, and LAVRENT'YEV (1961) studied the REE in pegmatites of northern Karelia. They found that the compositions of monazite and xenotime were constant throughout, but that the RE pattern of uraninite was dominated by Gd and Dy when this mineral formed in the presence of phosphate and by Dy-Er-Yb when phosphate was absent. Allanite was richer than normal in Ce when formed in the absence of phosphate. It was suggested that, in part, the REE were carried in solution as complex pyrophosphates.

SLEPNEV (1957) studied the lovchorrite-rinkolite pegmatites associated with the Khibinsk massif. He showed that while the common rock-forming elements (Si, Al, Fe, Ca, alkalis, etc.) are about equi-abundant in the pegmatites and the massif average, the pegmatites are enriched some 75 times in the REE. The RE content of the massif as a whole is about twice the crustal average. No RE minerals were found, but the REE were found to be concentrated in late stage minerals, including sphene, apatite, loparite, eudialyte, and lovchorrite. Significant amounts of REE were also found dispersed among K-feldspar, nepheline, arfvedsonite, and rinkolite.

## MINERALS

### RE and RE-concentrating Minerals

The earliest systematic studies of RE abundance patterns were made on minerals which for the most part have the REE as their essential constituents (GOLDSCHMIDT and THOMASSEN, 1924). Several characteristic

patterns or "assemblages" were recognized, based on which of the REE were predominant in a particular mineral. These observations were irrefutable testimony to the separation of the REE by natural processes, but did not seriously challenge the prevailing idea that this element group would retain its primordial distribution in the common rocks of the earth's crust. The patterns were designated as "selective" if either the Ce subgroup (La-Eu) or the Y subgroup (Gd-Lu+Y) strongly dominated the assemblage or as "complete" if no sharp difference in abundance between the Ce and Y subgroups was apparent. An example of a selective assemblage is that of the mineral monazite, in which the lightest lanthanides always strongly predominate. The assemblage found in apatite, a mineral in which the REE are not essential components, is described as complete, although the light REE again strongly dominate the assemblage. The strict categorization of RE patterns into "monazite type, selective" or "apatite type, complete" is rather arbitrary, as minerals exhibiting nearly all phases of variation between pattern domination by the lightest and the heaviest REE are known. However, most of the minerals in which the REE are necessary components do show considerable selectivity in their RE patterns because of structural differences between compounds of the light and the heavy REE, a result of the lanthanide contraction. For example, the common phosphate of the light REE is monazite. The corresponding phosphate in which the heavy REE predominate is xenotime, which has a different structure. In this sense, the selectivity in RE minerals is real. The details of the early studies on mineral RE assemblages are well summarized in the comprehensive works of GOLDSCHMIDT (1954) and RANKAMA and SAHAMA (1950). As has been pointed out by the latter writers, most of the RE minerals were of pegmatitic origin, and therefore are very special and representative of only a negligible portion of the REE in the earth's crust.

More important to the studies of RE distributions among the common constituent rocks of the crust are the RE minerals and those minerals which readily take up the REE and which occur as trace accessories in

ordinary igneous rocks. Numerous studies have been made of these minerals and the relationships of their distribution patterns to rock type and history. Earlier studies were concentrated on these minerals, and whole rock studies were neglected. There are several probable reasons for this. The minerals can be separated fairly readily from their host rocks. Their RE contents are high enough to allow satisfactory determination of the individual REE by standard analytical techniques. It seems to have been generally believed that when the RE patterns in these minerals were studied, the RE patterns in the whole rocks were also being studied. That this is not necessarily the case was indicated by the work of SAHAMÄ and VÄHÄTÄLO (1941). It was further emphasized by BALASHOV (1963a), and is supported by work discussed below. A comprehensive survey of the RE patterns of RE minerals proper and trace accessory minerals which contain significant amounts of these elements is in preparation (FLEISCHER, to be published) and thus will not be attempted here. Some of the more important, recent results on RE minerals are summarized below.

The notion of extreme selectivity in mineral assemblages has been weakened now that more analyses for the REE have been performed. For example, MURATA, ROSE, and CARRON (1953) and MURATA, et al. (1957), have shown that even in such selective minerals as monazite and allanite, there can be significant variations in RE pattern. They found it necessary to consider splitting the classical Y subgroup into smaller subgroups. VAINSSTEIN, TUGARINOV, and TURANSKAYA (1956) found three assemblages in monazites, two characteristic of pegmatites and one from carbonate and quartz veins. Similar variations were observed for xenotime and allanite. In his discussion of RE pattern variation in RE minerals and RE-concentrating minerals, BORODIN (1960) not only assails the concept of rigidly fixed selective assemblages, but also points out the inadequacy of rigidly classifying the REE into CE and Y subgroups. This was also concluded by SEMENOV and BARINSKII (1958). It is even truer

when whole rock patterns rather than RE minerals are considered. Borodin suggests the use of the terms "more basic" and "less basic," without strict assignment of the intermediate lanthanides to either class, but rather according to RE behavior in the particular system under discussion. In the present review, the REE are crudely designated as "light" and "heavy," with the latter group intended to include Y... Such methods are less convenient than the usual split into Ce and Y subgroups, but do not impose the problem of trying to make data fit an unwarranted classification.

LYAKHOVICH (1962) and LYAKHOVICH and BARINSKII (1961) have shown that there are notable changes in both RE contents and patterns in accessory minerals in high temperature granites and hydrothermal veins. Zircon and garnet from aplites, pegmatites, and quartz veins were found to be richer in REE than their counterparts in granitoids, while the reverse was true for apatites, epidotes, and fluorites. Also, the aplites and pegmatites are richer than the granitoids in total RE content, and contain a higher proportion of the heavy REE than do the granitoids, as judged from the relative abundances and RE patterns of the accessory minerals. In the quartz veins, the relative amount of heavy REE is less than in the granitoids. It was also found in the cases examined that most of the accessory minerals are syngenetic with the bulk rock, although it is possible to form such minerals either by magmatic crystallization or by the action of later solutions.

Most of the minerals whose RE contents are summarized in Table 26 were separated from biotite granites, but some were from two-mica and hornblende-mica granitoids. Some of Lyakhovich's comments regarding the RE patterns of these minerals are summarized below:

Monazite. This is the most common of the RE minerals which are encountered as an accessory in granitoids. It is strongly selective for the lightest lanthanides.

Allanite. This is the second most common accessory RE mineral and, like monazite, is strongly selective for the lightest lanthanides.

Table 26. Weight Per Cent REE in Accessory Minerals  
(Mostly from Biotitic Granites)<sup>a</sup>

Mineral	Minimum REE	Maximum REE
Allanite	2. 4	19
Apatite	0. 15	1. 1
Epidote	0. 16 o	3. 2
Fluorite	0. 4	2. 3
Garnet	0. 11	0. 6
Monazite	38	60
Sphene	0. 24	4. 0
Xenotime	---	50
Zircon	0. 13	5. 7

<sup>a</sup>Data from LYAKHOVICH (1962).

Xenotime. The RE pattern of accessory xenotime is always dominated by Y and the heavy lanthanides. The most abundant REE in accessory xenotime from granites is Dy, but Yb sometimes predominates in pegmatitic xenotime.

Fluorite. The light lanthanides dominate fluorite RE patterns, but the entire series of REE is always well represented.

Zircon. The heavy lanthanides and Y dominate zircon RE patterns, but the lighter lanthanides also are often found in considerable amounts.

Sphene. This mineral may be essentially devoid of REE. In all of the sphene from granitoids examined by Lyakhovich, the lighter REE were predominant, but Lyakhovich mentions reports of sphenes carrying principally Y and the heavier lanthanides.

Garnet. In aplites and pegmatites, the garnet patterns are invariably dominated by the heavier lanthanides and Y. In granites, garnet may carry significant amounts of the lighter REE as well. Some Ca-rich garnets are reported to contain mostly the lighter REE. The total RE content in garnets from some granites is very low.

Epidote. This is a secondary, postmagmatic alteration product of calcic plagioclase. The scant information available indicates that the light REE predominate, but one case where Y and the heavy REE were the most abundant has been reported.

Apatite. One of the most common accessory minerals in all varieties of granitoids, apatite usually contains more light REE than heavy REE.

Most of the above minerals contain Ca with coordination numbers from 7 to 9.

Lyakhovich comments that aside from the RE minerals proper, sphene and fluorite are the main concentrators of the REE in terms of total RE content. He found that in magmas the light REE are present in greater quantities than the heavier REE. Minerals which appear to be selective for the heavy REE in pegmatites usually turn out to be complete

in granites. Thus, the nature of the capturing mineral does not by itself determine the composition of its RE pattern. Rather, the pattern is influenced by the over-all geochemical character of the parent magma.

Lyakhovich also found a difference in accessory mineral RE content between fresh and altered granites. Garnets, apatites, and fluorites from greisenized or silicified granites are severely depleted in the REE. Zircons from albitized granites are strongly enriched in the heavy REE.

The RE patterns in the minerals from hybrid granites, which are characterized by xenoliths, abundant biotite and hornblende, zoned plagioclase more basic than normal for granites, and granodioritic gross compositions, were found to have higher RE contents, more dominated by the light lanthanides, than those of unaltered biotite granites. It is suggested that the high mineral RE contents of hybridized granites might serve to distinguish these granites from similar rocks of intermediate composition which were products of magmatic differentiation or alteration of basic rocks, and for which the RE contents are much lower.

The behavior of the REE during mineral alteration of allanite was also studied by MINEYEV, MAKAROCHKIN, and ZHABIN (1962). They found that the REE Sm-Dy were the most mobile and tended to be concentrated in the alteration products. The mobilities of the heavier REE increased with increasing acidity of the mineralizing solutions. By contrast, ZHIROV, GANDURKIN, and LAVRENT'YEV (1961) found that the alteration of pegmatitic allanite removed the lightest lanthanides selectively, and did not appreciably change the amounts of heavy REE and Y in the mineral.

SEMENOV (1957, 1958) has sought explanations for the selective nature of RE minerals. He points out that in RE minerals a solid solution of several isovalent RE cations is involved. However, not all the REE are equally acceptable to a particular lattice arrangement. An extreme case is  $\text{CePO}_4$  (monazite) and  $\text{YPO}_4$  (xenotime), whose structures are not isomorphous. Apatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl})$ , permits entry of both light and

heavy REE, thus yielding a complete assemblage. Semenov notes that selectively light RE minerals usually have cation coordination numbers of 10 to 12, and in minerals selectively favoring Y and the heavy lanthanides the coordination number is close to 6. Minerals with complete assemblages have intermediate coordination numbers. These minerals appear to be capable of varying their lattice dimensions sufficiently to accommodate a wide range in ionic radius of accepted ions. Semenov reports an observed variation of 56 per cent in the apatite unit cell, but that no increase beyond 10 per cent has been found for minerals of the alumite-florencite group with a coordination number of 12. He predicts that calcite (coordination number of 6) would not accept as much REE as aragonite (coordination number of 12).

Semenov shows that in minerals which are selective for the light REE, the log of the abundances of the even-Z (or odd-Z) elements decreases approximately linearly with increasing atomic number. He attributes such behavior to a strict requirement for similarity of ionic radius between the principal lattice cation and the cation being admitted. This phenomenon he restricts to the most selective minerals with the extremes in coordination number, with isomorphism involved in the minerals which admit complete assemblages. No sharp boundary is expected between the processes, however.

Semenov suggests that the most important quality of a "capturing" mineral would be close similarity in ionic radius to the ion to be captured. He states that Sr, Ba, K, and Na minerals are generally selective for the light REE, and Fe, Zr, Sc, and Mn minerals are selective for the heavy lanthanides and Y. He regards Ca as not especially favoring one RE group over another. However, re-examination of these statements in the light of more recent data does not bear out this simple classification.

Semenov presents an interesting concept of "mean effective ionic radius" for the lanthanides which, for a particular assemblage, is an average ionic radius based on the ionic radius of each element weighted according to the relative abundance of that element in the assemblage.

The REE, then, would have to adjust from their relative proportions in a melt or solution to be within the permitted range of mean effective ionic radius for a crystallizing mineral.

Much further and crucial insight into the effects of ionic radius and coordination number on the patterns of the REE in minerals is given by KHOMYAKOV (1963). He notes from observation and published data on natural and synthetic RE compounds that the limits in variation of RE composition are influenced not only by ionic radius and coordination number, but also by the RE content. Khomyakov points out that the dependence described by SEMENOV (1957) of selectivity for light RE in minerals of coordination numbers near 12 and selectivity for Y and the heavy lanthanides in minerals of coordination number 6, is not entirely general. An outstanding exception is monazite, which, although it is strongly selective for the lightest lanthanides, has a coordination number of 9 and would be predicted to yield a complete, rather than a selective, assemblage. The interdependence of selectivity, ionic radius, and cation coordination number can be shown as follows.

Cerium sesquioxide,  $\text{Ce}_2\text{O}_3$ , is trigonal in structure and has a coordination number of 9. Yttrium sesquioxide is isometric with a coordination number of 6.  $\text{CePO}_4$  (monazite) is monoclinic with a coordination number of 9, and  $\text{YPO}_4$  (xenotime) is tetragonal with a coordination number of 8. Finally,  $\text{Ce}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Y}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  are both orthorhombic with a coordination number of 8. From the above compounds it becomes apparent that the influence of the REE on the crystallochemical properties of their compounds decreases as their mole fractions in those compounds decrease. The dimensions of the unit cell become less dependent on the size of the RE ion involved, and the individual REE can be more readily interchanged and substituted. Hence, in nature those minerals, such as monazite and xenotime, with high mole fractions of REE tend to be very selective. In minerals where interchange of REE cannot produce marked effects on the volume of the unit cell, a

wider variation in RE assemblage is observed. For example, euxenite,  $\text{Y}(\text{Ti}, \text{Nb})_2\text{O}_6$ , and eschynite,  $\text{Ce}(\text{Ti}, \text{Nb})_2\text{O}_6$ , are considerably less selective than monazite and xenotime. The same is true for apatite and sphene.

The data show that sphene has a higher capacity for heavy than for light REE. The opposite is true of apatite. It is observed that in nepheline syenites, which are relatively rich in the light REE, apatite has a higher RE content than sphene. The opposite is true for those granites in which the heavy REE are more abundant. An increase in total RE content with a shift from light to heavy REE has been observed for eudialyses and pyrochlores. Highest RE contents for sphene, fluorite, garnet, and davidite are found in the varieties with greatest heavy RE predominance. Perovskites, epidote, allanite, and other minerals increase in total RE content as their assemblages become more dominated by the lightest REE.

In epidote, half of the Ca can be replaced to give allanite,  $\text{CaREFeAl}_2(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O(OH)}$ . Epidote has a lower capacity for heavy than for light REE, so that the heavy REE are less capable of replacing Ca than are the light REE. In fact, allanites with relatively high proportions of Y and the heavy lanthanides seldom contain more than ~15 per cent REE, whereas the varieties which are most strongly dominated by the light REE contain as much as 25 per cent REE. The opposite trend is found in the case of fersmite-euxenite,  $\text{CaNb}_2\text{O}_6 - \text{Y}(\text{Ti}, \text{Nb})_2\text{O}_6$ .

Khomyakov states that the differences in capacity for acceptance of the REE among minerals depend strongly on the nearness of the ionic radii of the substituting cation and the one being substituted. Then, coordination number effects become important. For example, minerals in which Ca has coordination numbers from 8 to 12 (apatite, epidote, perovskite, etc.) have a higher replacement capacity for the light REE, and those with Ca coordination numbers from 6 to 8 (sphene, fluorite, etc.) are more favorable to replacement by the heavy REE. Komyakov stresses the important point, too often overlooked in discussions of diadochic substitution, that the ionic radius of a particular cation is not a

fixed quantity, but depends on the crystal environment. For this reason, different members of the RE group substitute best for the same ion, Ca, in different compounds.

In the series M = Ca, Sr, Ba, there is an increase in the interatomic metal-oxygen distance in going from the oxide MO (coordination number of 6) to MTiO<sub>3</sub> (coordination number of 12). The increase for Ca is ~12 per cent, that for Sr is ~7 per cent, and that for Ba is only ~3 per cent. If the 3 per cent correction for Ba is used to "correct" the ionic radii of the lanthanides to a coordination number of 12, the corrected ionic radii of the lightest lanthanides most closely approach that of Ca at a coordination number of 12. The smaller radius of Ca at a coordination number of 6, however, is most similar to that of the heavy lanthanides and Y. Thus, the change in preference by Ca for different elements of the RE group arises in a natural way from the effect of changing lattice environment on cation ionic radius.

FLEISCHER (1965a, b), on careful examination of all the available data for RE minerals, succeeded in demonstrating that both crystallochemical factors and geochemical environment influence the average RE patterns in minerals. He emphasized the word "average," since some overlap was found among individual patterns for a given mineral from the several rock types considered. When the average ratios of La/Nd were plotted against the  $\Sigma$ La + Ce + Pr for groups of monazites from different rock types, a clear trend of decrease in both parameters was noted in the order carbonatites, alkalic rocks, quartz veins, granites, granite pegmatites, cheralite granite pegmatites. A similar dependence on rock type was found for allanites, epidotes, apatites, and britholites. A qualitative positive correlation between the contents of the heavy REE and Ca was found among similar minerals.

#### Rock-forming Minerals

Studies of REE incorporated in or inseparably associated with the rock-forming minerals show clearly that the RE pattern of a rock is not

necessarily always, or even usually, the same as that of its accessory minerals. Careful studies on the separated major minerals of the Kirovograd granite were made by GAVRILOVA and TURANSKAYA (1958). Partial RE analyses were performed for five mineral fractions, including monazite, apatite, and garnet. The mineral RE contents are given in Table 27 and the whole rock distribution appears in Fig. 23. GAVRILOVA and TURANSKAYA (1958) and CORYELL, CHASE, and WINCHESTER (1963) attempted to estimate the fraction of the total rock content of each REE which is associated with each mineral, with the following conclusions. Monazite accounts for about 60 per cent of the elements La-Sm, and the RE relative distribution pattern for that mineral is about the same as that of the whole rock for the light REE. A very negligible portion of the light REE in the rock is present in apatite, but as much as 20-30 per cent of the heavy REE are found in that mineral. The feldspar and quartz fraction contains about 30 per cent of the light REE and has a distribution pattern similar to that of the whole rock. Biotite and chlorite contain less than 10 per cent of the light REE, but possibly contain about 30 per cent of the heavier REE. Garnet, a selective mineral for heavy REE, appears to contain at least 30 per cent or more of the heavy REE in the rock. The values for the heavy REE are uncertain because the data are not complete.

A more nearly complete study of RE mineral patterns was made by TOWELL, WINCHESTER, and SPIRN (1965) on the gabbro of the southern California batholith. The results of their analyses of mineral fractions are given in Table 27 and are shown in Fig. 34, where instead of the arbitrary normalization to chondrites, the absolute RE content of each mineral has been normalized to that of the whole rock. Thus, the ordinate of Fig. 34 gives the fraction of the whole rock content which is contributed by each mineral for each REE. From 80 to 100 per cent of the REE in the San Marcos gabbro is accounted for in the mineral fractions analyzed. There are considerable differences in RE pattern among the component minerals. Except for La and Eu, the bulk of the REE in the rock is contained

Table 27. REE Contents of Rock-forming Minerals (ppm)

	Japanese Eclogite <sup>a</sup>		San Marcos Gabbro <sup>b</sup>				Rushveldt Norite <sup>c</sup>		Wausau Syenite Peg. <sup>d</sup>	
	Garnet	Pyroxene	Plagioclase	Hornblende	Augite	Apatite	Mafic	Felsic	Arfvedsonite	Feldspar
La	0.82	5.1	2.3	2.4	0.41	390	6.1	6.8	270	34
Ce	2.2	12.6	3.6	---	---	---	6.1	10.4	---	---
Pr	0.20	1.6	---	---	---	170	0.6	1.15	109	10.1
Nd	1.5	7.2	---	---	---	530	---	4.9	380	36
Sm	1.7	1.7	0.26	9.0	4.4	97	0.92	0.64	127	7.0
Eu	1.04	0.50	0.81	2.1	0.92	17	0.15	1.20	21	2.9
Gd	3.3	0.74	---	---	---	---	1.11	0.47	88	6.4
Tb	0.57	0.065	---	1.8	1.32	12.5	0.35	0.04	---	1.04
Dy	---	----	0.17	13.1	7.8	67	---	---	---	---
Ho	0.85	0.024	0.048	2.5	1.5	13.5	0.30	0.05	14.6	0.84
Er	2.6	0.051	---	---	---	---	0.95	0.15	40	1.6
Tm	0.36	0.0056	0.022	1.20	0.69	3.3	0.17	0.02	6.0	---
Yb	3.0	0.041	0.15	7.7	4.0	20	2.1	0.05	35	0.98
Lu	0.49	0.012	0.023	1.07	0.74	3.1	0.34	0.035	6.8	0.17
Y	20	0.54	1.08	73	44	30	7.7	0.63	170	16
$\Sigma$ REE	41	30	9.5	130	85	2,600	28	26	1,800	180

Table 27 (continued)

	Neillsville Gneiss <sup>d</sup>		Rubiodoux Mt. Leucogranite <sup>b</sup>			Kirovograd Granitee <sup>c</sup>				
			Plagioclase	Potassium Feldspar	Biotite	Feldspar	Biotite	Garnet	Apatite	Monazite
	Mafic	Felsic								
La	83	52	10.7	9.7	230	23	139	---	280	130,000
Ce	---	---	---	---	---	50	270	14	1,000	230,000
Pr	14.7	9.3	---	---	68	4.5	35	---	200	22,000
Nd	52	23	---	---	220	19	135	11	920	90,000
Sm	6.4	3.6	1.7	1.07	48	3.5	29	4.5	350	15,500
Eu	0.73	0.96	0.97	0.94	0.36	---	---	---	---	---
Gd	---	2.5	---	---	---	---	21	27	450	12,000
Tb	0.31	0.25	---	---	7.3	---	---	---	115	---
Dy	---	---	1.7	0.74	43	---	---	74	400	---
Ho	0.57	0.35	0.45	0.17	9.6	---	---	14	100	---
Er	1.17	1.06	---	---	---	---	---	53	146	---
Tm	0.28	0.16	---	0.078	3.2	---	---	---	---	---
Yb	1.01	0.82	0.90	0.51	22	---	---	.26	---	---
Lu	0.17	0.17	0.129	0.068	2.7	---	---	4	---	---
Y	12.4	10.5	8.5	4.7	230	---	---	26	1,460	---
$\Sigma$ REE	330	200	60	35	1,500	>100	>630	>230	>5,400	>500,000

<sup>a</sup>FREY and HASKIN (1965).<sup>b</sup>TOWELL, WINCHESTER, and SPIRN (1965).<sup>c</sup>FREY, HASKIN, and POETZ (1965).<sup>d</sup>GEHL (1964).<sup>e</sup>GAVRILOVA and TURANSKAYA (1958).

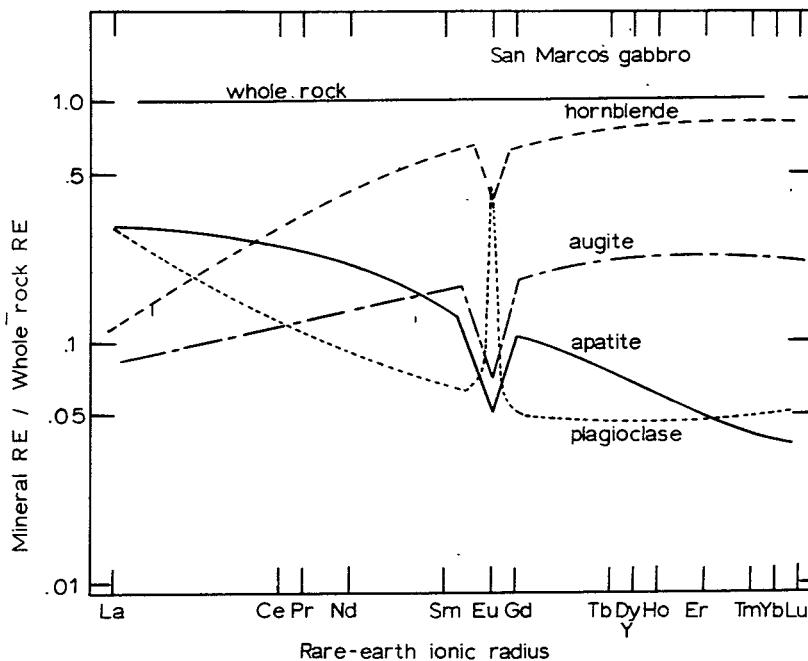


Fig. 34. Comparison plot for minerals of the San Marcos gabbro (Table 27). The unnormalized RE contents of the minerals have been divided by the RE content of the whole rock, rather than by the pattern for chondritic meteorites. Note the strong preference of Eu for the feldspar.

in the dark minerals. The feldspar, with its much lower RE content, favors the light REE over the heavier ones. The anomalously high Eu content of the feldspar is most remarkable. Although the feldspar contains well under 10 per cent of the heavier REE, it contains nearly 50 per cent of the Eu, such a high proportion that Eu is relatively depleted in the other three minerals. The San Marcos gabbro as a whole has an anomalously high Eu content (Fig. 18). This could occur because of the very high Eu content of the feldspar even if the apatite, hornblende, and augite had normal amounts of Eu relative to their neighboring elements. However, normalization of these minerals to chondrites shows that the Eu contents of the augite and hornblende are anomalously low relative to a "normal" pattern, and this indicates that there was an actual competition for the Eu among these minerals during their formation. Whether there is a Eu anomaly for the apatite relative to a normal distribution is not certain. WICKMAN (1943) suggested that divalent Eu should follow Sr into feldspars, and HABERLANDT (1947) believed that not only Eu but also Yb and possibly Sm had been separated by natural processes from the other REE as divalent ions. There is no recent evidence to support such a separation for Sm or Yb.

About half of the REE in the Rubidoux Mt. leucogranite is accounted for in the mineral fractions analyzed (Table 27, Fig. 35). Again, the feldspars show very marked anomalous enrichment in Eu. This is definitely at the expense of the biotite and other minerals, since the rock as a whole is deficient in Eu, relative to a "normal" pattern, as judged by the abundances of the neighboring elements. It is interesting to note that there is less variation in RE pattern among the component minerals than was found in the gabbro. The K-feldspar slightly favors the lighter REE and the plagioclase slightly favors the heavier REE, relative to the whole rock pattern. The light REE are somewhat more predominant in the whole rock than they are, on the average, for the earth's crust.

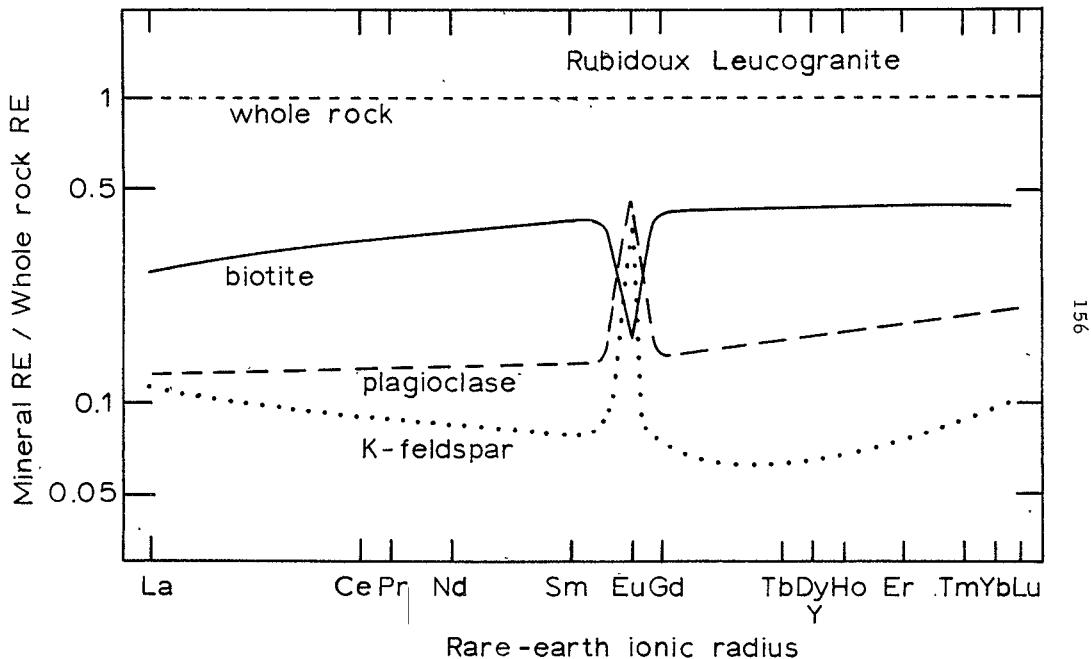


Fig. 35. Comparison plot for minerals of the Rubidoux Mt. leucogranite (Table 27). The un-normalized RE contents of the minerals have been divided by the RE content of the whole rock.

The Bushveldt norite was separated into light and dark mineral phases for RE analysis (FREY, HASKIN, and POETZ, 1965). The light phase, principally plagioclase feldspar, has about the same concentration of REE as the dark portion, but has a somewhat higher fraction of the lighter REE and most of the Eu.

In the Neillsville gneiss (GEHL, 1964), the RE patterns for the light and dark mineral fractions are approximately the same except for Eu, which is again relatively enriched in the light phase. The RE content of the dark minerals is somewhat greater than that of the light minerals. The whole rock distribution was not determined, but is relatively richer in the light REE than the crustal average.

In a pegmatite of over-all syenitic composition, nearly all the REE were found to be associated with the dark minerals (mostly arfvedsonite) (GEHL, 1964). The light (feldspar) fraction was relatively richer in the light REE and anomalously rich in Eu. The total amount of REE, including Eu, in the light fraction was so small, however, that no Eu depletion could be observed in the dark mineral. The whole rock pattern was not determined, but is essentially that of the dark minerals and is similar to the crustal average.

A very striking example of REE partition between rock-forming minerals is the Japanese eclogite. The whole rock pattern is similar to that of chondrites (Fig. 36). The pyroxene contains most of the light REE, and the heavy REE are contained in the garnet. There is no noticeable Eu anomaly. This partition is intriguing because of the suggestion of YODER and TILLEY (1962) that crystallization of garnet from an eclogitic liquid would leave a liquid phase with a composition similar to alkali basalt, and crystallization of pyroxene would leave behind a liquid of tholeiitic composition. If such a process had influenced the source materials of oceanic tholeiitic basalts and the alkali basalts examined, the difference in RE patterns (Figs. 6, 7, 14) between the two basalt types could be readily explained. However, the sample of Columbia plateau tholeiite has a REE

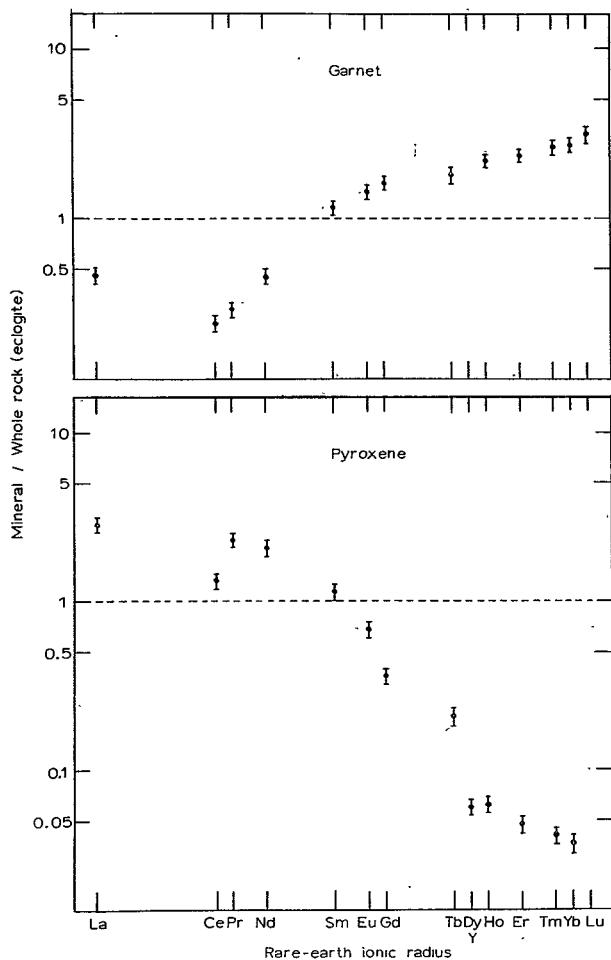


Fig. 36. Comparison plot for minerals of the Japanese eclogite (Table 27). The unnormalized RE contents of the minerals have been divided by the whole rock RE contents. Note the severe partition of the light and heavy REE between the minerals.

pattern (Fig. 6) like that of the alkali basalts, so no such simple explanation covering the difference between tholeiitic and alkali compositions is possible. Nevertheless, such selective RE partition among major minerals is a very efficient way of separating the REE and is probably an important process for causing their fractionation in nature.

The present data on RE distributions and contents of rock-forming minerals give rise to several conclusions:

1. The amount of REE incorporated in or inseparably associated with the rock-forming minerals is a significant fraction of, and may include the bulk of, the REE in the rock.
2. There is considerable fractionation among the RE group as a result of RE partition among the rock-forming minerals.
3. The mafic minerals tend to have higher REE concentrations than the felsic minerals and tend to favor the heavier REE.
4. The felsic minerals exhibit a preference for the lighter REE and a strong anomalous preference for Eu.

#### SEDIMENTARY ROCKS

##### Survey; Mixing Effects of Sedimentary Processes

The first careful analyses of the REE in sedimentary rocks were made by MINAMI (1935), who analyzed three composite samples of Japanese and European shales by x-ray spectrography. Minami found substantially the same RE pattern in all three composites. There is some question about the absolute RE contents of these samples. The sum of the weights of the individual REE in no case is the same as the weight of the RE oxide group as determined gravimetrically. Minami suggested that in at least two of the cases, Ba might have been present in the gravimetric determinations. The average values from the three analyses are given in Table 28, and the total RE content has been estimated from the gravimetric data. Preliminary neutron activation data on a sample believed to be one

Table 2.8. RE Contents of Some Composite Sediments (ppm)

	European and Japanese Shales <sup>a</sup>	Finnish Sediments <sup>b</sup>	40 North American Shales <sup>c</sup>	Russian Platform Avg. <sup>d</sup>
La	18	13.6	39	50
Ce	46	20	76	98
Pr	5.6	4.3	10.3	12
Nd	24	13.6	37	44
Sm	6.5	3.4	7.0	9.5
Eu	1.07	---	2.0	---
Gd	6.4	4.7	6.1	7.8
Tb	0.91	---	1.30	1.8
Dy	4.5	3.0	----	6.2
Ho	1.21	---	1.40	1.8
Er	2.5	1.8	4.0	4.3
Tm	0.20	---	0.58	---
Yb	2.7	1.31	3.4	4.2
Lu	0.66	---	0.60	---
Y	28	11	35	49
$\Sigma$ REE	148	>77	240	280

<sup>a</sup> MINAMI (1935).<sup>b</sup> SAHAMÄ (1945).<sup>c</sup> HASKIN, et al. (1965b).<sup>d</sup> BALASHOV, et al. (1964).

of the composite shales analyzed by Minami show that the actual RE contents are much higher than either the sum of the individual REE or the gravimetric determination indicates (POETZ and HASKIN, 1966).

Minami's results were interpreted by GOLDSCHMIDT (1938), who called attention to two particular features of the shale distributions. All three shales have essentially identical patterns, and in all three the element Eu is present in an abundance which is similar to that of the other odd-Z REE, unlike the minerals examined by GOLDSCHMIDT and THOMASSEN (1924) in which Eu was markedly depleted relative to its odd-Z neighbors. Anomalous enrichment of Eu in Sr and Pb minerals had also been observed by Goldschmidt and Bauer (GOLDSCHMIDT, 1937, 1938). Goldschmidt concluded that the processes of weathering and sediment formation which produced the shales had again mixed the REE, previously differentiated somewhat by igneous processes, back into their crustal (and perhaps primordial) relative abundance distribution. Since their publication, Minami's values have been used as the source material for nearly all compilations of crustal abundance.

Relative RE abundance patterns very similar to those found by Minami were obtained for a quartzite and two composite shales by SAHAMA (1945). The averaged RE contents of the shales are given in Table 28. The quartzite pattern is relatively a little richer in La and Ce than the shale patterns. Sahama attributed the RE pattern of the quartzite to trace monazite, which has a selectively La- and Ce-rich pattern and which, as a result of his studies on granites from the same region, he expected would be present. The shales were thought to have derived principally from basic rocks, but their RE patterns did not resemble those of the Finnish basic rocks (Fig. 16) presumed to be their source. The absolute RE contents of the basic rocks were very low; however, so Sahama proposed that most of the REE found in the shales was of granitic origin, even though the bulk of the major elements of the shales came from basic material.

The RE contents of ten individual sedimentary rocks were determined by HASKIN and GEHL (1962). Seven of the ten were found to have very

similar RE relative abundance patterns, and the remaining three were declared to be anomalous. The average of the seven similar patterns generally resembled the distribution reported by MINAMI (1935) and was taken to be an improved measurement of the relative abundances of the REE in the earth's crust. A somewhat surprising discovery made as a result of this work is that the RE patterns--not from composites of shales but from hand specimens of limestones, sandstones, shales, and their metamorphic equivalents--were all very similar to the crustal average. Apparently the geochemical separations involved in producing sediments of widely different chemical character have no drastic effects on relative RE distributions. The metamorphism of limestone to marble, and of sandstone to quartzite, also did not effect any major changes in the relative RE distributions.

The REE in a New Mexico (Todilto) limestone were analyzed by Breger (GRAF, 1960), and the RE pattern was found to be similar to that of other limestones.

Although the similarity in RE patterns among the sediments was stressed, it was pointed out the individual patterns were slightly different from each other outside of experimental uncertainty, even among the seven used to obtain the average. It was suggested that the three anomalous RE patterns, all from Precambrian sediments, might have resulted from selective leaching, or might actually reflect a lesser homogeneity of the earth's crust early in its history.

WILDEMAN and HASKIN (1965) analyzed eight ocean sediments following the report of GOLDBERG, et al. (1963), in which it was shown that the RE patterns for ocean water were distinctly different from that previously found for sedimentary rocks, some of which were presumably of marine origin. Three Atlantic and two of five Pacific sediments yielded RE patterns indistinguishable from the average of the continental sediments. The other three Pacific samples, while different from the continental sediment average, showed no systematic deviations from that average.

which could lead to interpretation in terms of a plausible chemical process. The average of the eight ocean sediment patterns agreed, within the experimental uncertainties of  $\pm 10\text{-}15$  per cent, with the continental sediment average. Essentially the same pattern was reported by OSTROUMOV (1953) for sedimentary material from the Black Sea.

HASKIN, et al. (1965b), obtained analytical values for the REE in 16 additional sediment samples and in a composite of 40 North American shales. They then attempted to re-evaluate the average pattern for sediments and to look for differences in average REE patterns among different sediment types. In this work, none of the sediment REE patterns obtained was arbitrarily omitted from the average for its type, as had been done in previous work (HASKIN and GEHL, 1962). The REE patterns of the composite of 40 shales, the average of 34 individual samples of limestone, sandstone, shales, greywackes, and ocean sediments, and seven of those 34 which had been averaged in the previous work were mutually indistinguishable to within the  $\pm 10\text{-}15$  per cent experimental uncertainty. The composite of North American shales was arbitrarily selected as providing the best approximation of the average REE pattern of that part of the earth's crust which is subjected to the weathering cycle. The REE patterns of the 34 individual specimens were then compared with the shale pattern. It was found that even though the average of the 34 patterns matched the shale pattern, only seven of the 34 individual patterns were identical to it within experimental error. The number of individual patterns in agreement with the shale pattern is given as a function of sediment type in Table 29. As an example of the variation among individual sediment patterns, the patterns of the five greywackes are shown in Figs. 37 and 38. The only class of sediments for which a significant number of patterns agreed with the shale pattern is the ocean group. This probably is a result of superior mixing of material from a wider area in the production of this class.

Even though relatively few of the individual patterns agreed with the shale pattern, the averages of the patterns of the five sediment classes

Table 29. Number of Sediment RE Patterns According to Type, and Number Identical With North American Composite Shale Pattern<sup>a</sup>

Type	Number of Patterns	Number of Patterns Identical With Shale Pattern
Sand	5	1
Carbonate	8	0
Shale, Clay	8	1
Greywacke	5	0
Ocean	8	5
Total	34	7

<sup>a</sup>HASKIN, et al. (1965b).

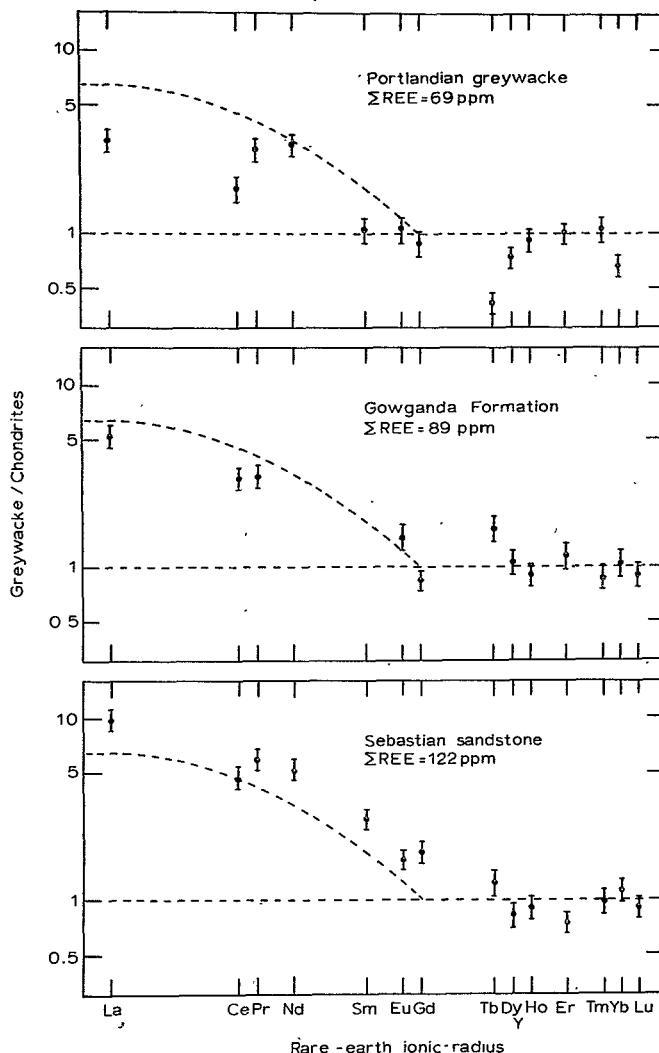


Fig. 37. Comparison plots for greywackes. Upper dashed curve represents the North American composite shale.

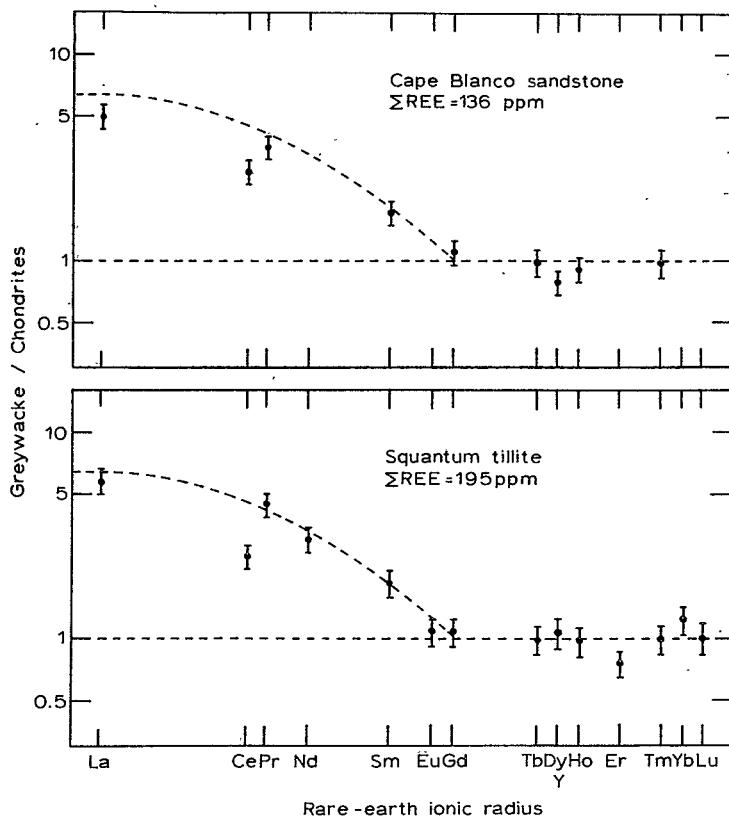


Fig. 38. Comparison plot for greywackes.

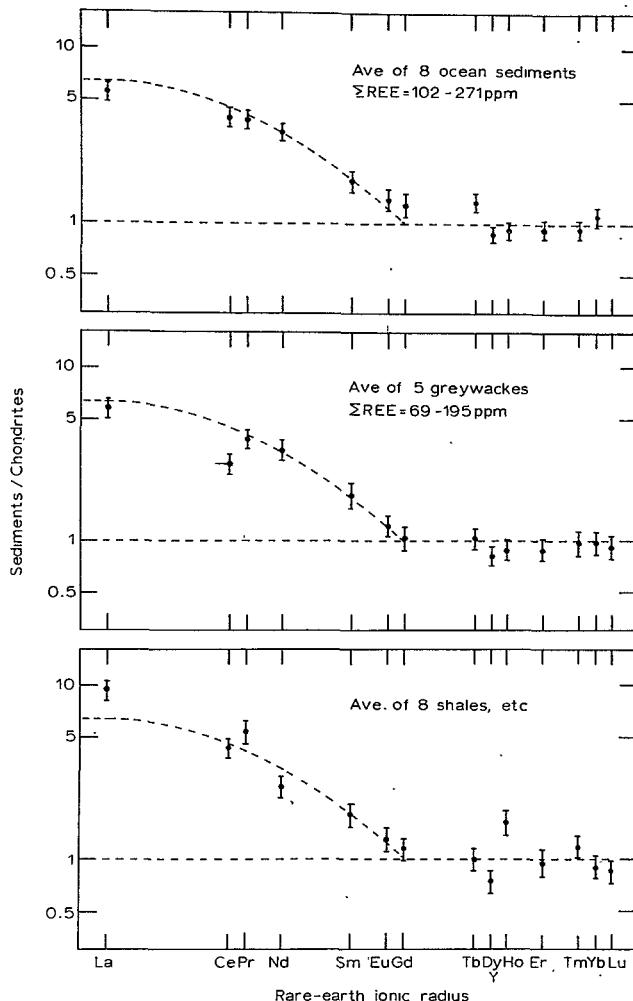


Fig. 39. Comparison plot for pattern averages of five greywackes, eight shales, and eight ocean sediments (Table 30). Upper dashed curve represents the North American composite shale.

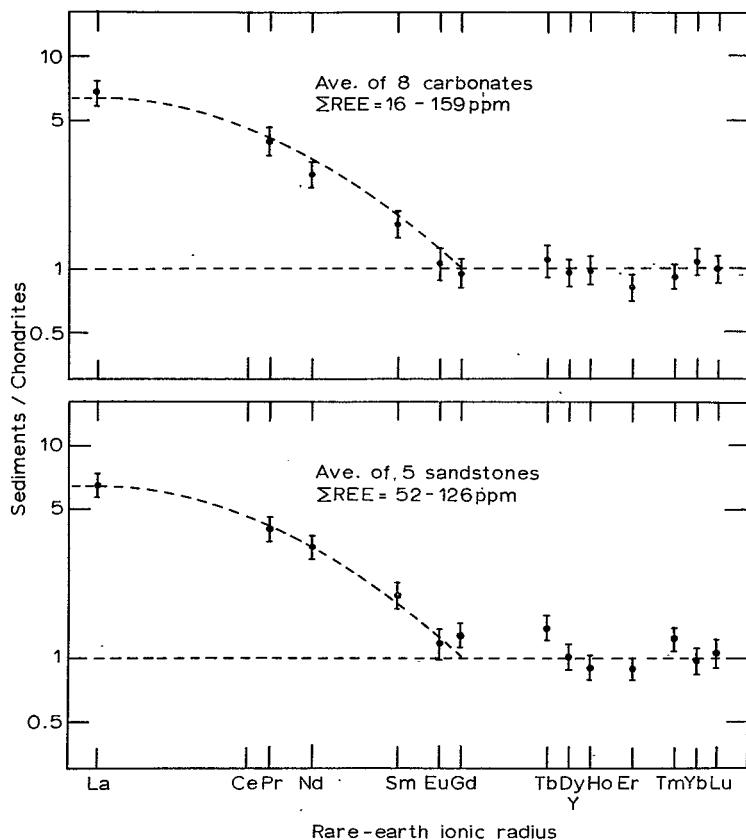


Fig. 40. Comparison plot for pattern averages of eight carbonate rocks and five sandstones (Table 30).

Table 31. Number of Individual RE Values among 412 from 34 Sedimentary RE Patterns Which Deviate by a Given Percentage from the North American Composite Shale RE Pattern<sup>a</sup>

Deviation (per cent)	Number of RE Values	Fraction of Total RE Values (per cent)
±50-100	42	10
±100-200	16	4
±200	4	1
Total	62	15

<sup>a</sup>HASKIN, et al. (1965b).

Table 32. Number of Sediment RE Patterns According to Range of Deviation of Most Aberrant Value From the North American Composite Shale Average<sup>a</sup>

Deviation (per cent)	Number of Patterns	Fraction of Total Patterns (per cent)
±50-100	15	44
±100-200	7	21
±200	3	9
Total	34	74

<sup>a</sup>HASKIN, et al. (1965b).

numbers differing from the shale values by 1.5 to 2 times, by 2 to 3 times, and by more than 3 times are recorded in Table 28. For each of the 34 sediments, the extent of deviation of the single, most aberrant element in the pattern is recorded in Table 32. From Table 32 it is seen that only about one-fourth of all the sediment patterns are similar enough to the composite shale that no single element deviates by as much as 1.5 times. In fact, nearly one-third of the patterns have at least one element which differs from the shale by a factor of 2 or more. Examination of the graphs for the individual sediments showed that many of the aberrant values are undoubtedly due to experimental error, since they occur for elements which stand widely apart from their neighbors in the pattern trend, but for which, unlike Ce and Eu, there is no known geochemical means of selectively concentrating or depleting. The rest of the deviant values are real and reflect trends of difference between the sediment under examination and the crustal average.

Really large deviations of individual sediment patterns from the crustal average are much rarer than the values in Table 32 seem to imply, as is shown in Table 31. Only 15 per cent of the 412 individual RE values deviate by as much as 50 per cent (1.5 times) from the composite shale pattern, and deviations as great as a factor of 2 are found only for one value out of 20. It just happens that the relatively few, highly deviant values are very well scattered among the 34 sediment patterns. Thus, HASKIN, *et al.* (1965b), concluded that the individual sediments do differ from the crustal average by amounts exceeding experimental error, but that trends leading to deviations as great as a factor of 2 are rare, involving not more than 5 to 10 per cent of the individual samples.

Literature values for the REE in sediment composites are available from four groups of analysts. The RE contents of these composites are given in Table 28, and the RE patterns are compared to that of the composite of North American shales in Fig. 41. Also included in Fig. 41 is the average of 34 individual sediment patterns discussed above. HASKIN, *et al.*

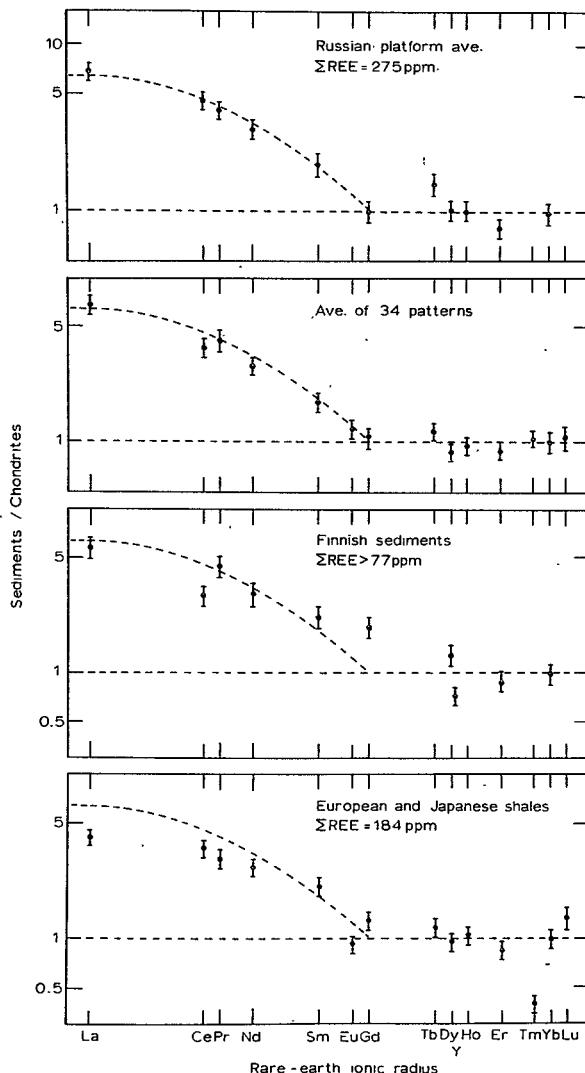


Fig. 41. Comparison plot for four sediment composites (Table 28). Upper dashed curve represents the North American composite shale.

(1965b), state that for standard deviations of 5 to 10 per cent, the American shale composite, the average of 34 individual patterns, and the Russian Platform average are identical in RE pattern. The other two samples are similar to, but not identical with, these three, but they were determined by less accurate analytical methods than are now available. In particular, very pure samples of the individual REE to serve as standards were lacking. Thus, it seems very well established that the relative RE abundance pattern of the composite of North American shales, the average for 34 individual sediments, and the Russian Platform is an accurate representation of the average RE pattern of the earth's crust, or at least of that part of the crust which is engaged in the weathering cycle. However, attention is called to the fact that the pattern obtained by MINAMI (1935) shows a definite trend of less relative enrichment in the light REE than the other four patterns display, and this trend is not necessarily a result of experimental error.

It is considerably more difficult to determine the absolute RE content of the crust or of shales than to obtain the relative RE abundances. The average for Russian Platform clays (BALASHOV, *et al.*, 1964) is 335 ppm, while that for the American shale composite is 275 ppm. The older determinations of Minami and Sahama gave much lower values, 184 ppm and >74 ppm, respectively. These low values may be due to experimental error, as discussed previously. The absolute RE contents reported by Sahama for granites and gabbros are also very low compared with more recent values. Again, this is probably due to experimental error, but may reflect an actual lower absolute abundance for the REE in the area of Finland which was sampled.

#### Russian Platform; Separation Effects of Sedimentary Processes

Some geochemical implications of the variability which is observed among sediment RE patterns have been brought out in an excellent investigation of REE in sediments by BALASHOV, *et al.* (1964). These workers

selected representative materials from the extremes of arid and humid conditions of sediment formation from the tectonically relatively quiet Moscow syncline of the Russian Platform, of middle Paleozoic age. In the Famensk stage of development, sediments were formed under ever-increasing aridization of the climate. The basin became progressively saline, and there was some increase in tectonic activity in the zones of feeding. Mineralogically, the sediments are rather monotonous. In the Jasnopoliansk substage, there was tectonic calm, but a hot, humid climate prevailed. This resulted in a regular zonality of the sediments in the basin, with a sharp differentiation of deposits, yielding monomineralic quartz associations in the sandstones, kaolinite clays, and bauxites. Average specimens of clay, sandstone, and carbonate along the facies profile were analyzed for the REE.

Average RE contents for the sediments of the Famensk stage are given in Table 33, and the distribution patterns for the clays and sandstones are shown in Figs. 42 and 43. From Fig. 42 it is seen that the RE patterns of the clays from both the continental and lagunal environments are nearly the same, although there is a slight decrease in the relative heavy REE content and in the total RE content of the clays from the continental to the lagunal environment. The RE content of the sands decreases slightly from the continental to the lagunal environment, but there is an increase in the relative content of the heavy REE. The absolute RE content of the Famensk sandstones exceeds that of the clays. On the whole, the sediments of the Famensk stage are characterized by constancy of RE content and distribution pattern.

In the Jasnopoliansk basin, considerable differentiation was observed in the RE contents and distribution patterns of all the rocks (Table 30, Figs. 43 and 44). The highest RE contents were found in the clays of the continental, variegated zone, adjacent to the areas of ablation. Deeper in the basin, in the direction of coal-bearing formations, the RE content of the clays decreases to the minimum value for the basin. The RE

Table 33. RE Contents of Some Russian Platform Sediments (ppm)<sup>a</sup>

	Famensk Basin						Jasnopoliansk Basin		
	Clay, Continental, Arid 71	Clay, Saline, Lagunal 70	Sand, Continental, Arid 38	Sand, Saline, Lagunal 38	Sand, Basin Average 76	Clay, Basin Average 141.	Clay, Continental, Variegated 69	Clay, Coal-bearing Formations 45	Clay, Seacoast, Humid 34
La	48	41	57	45	51	44	79	58	58
Ce	89	81	105	81	93	84	150	113	118
Pr	12	11	14	12	12	11	19	14	15
Nd	44	38	47	39	43	40	63	50	60
Sm	11	8	10	10	9.8	9.2	12	10	14
Eu	--	--	--	--	--	--	--	--	--
Gd	9	6.6	10	8	9.0	7.7	10	7.6	12
Tb	--	--	--	1.9	2.0	--	--	2.0	--
Dy	7	6.4	8.4	10	9.2	6.9	7	5.6	9
Ho	--	--	--	2.0	2.2	--	--	1.5	--
Er	5.8	4.4	5.9	6.0	6.0	4.9	4.7	3.5	6
Tm	--	--	--	--	--	--	--	--	--
Yb	5.4	4.3	5.5	5.3	5.6	4.8	4.2	3.1	6
Lu	--	--	--	--	--	--	--	--	--
Y	66	45	61	69	65	54	51	40	65
$\Sigma$ REE	300	260	330	290	310	280	420	300	360

<sup>a</sup>BALASHOV, et al. (1964).

Table 33 (Continued)

	Jašnopoliansk Basin					Platform Averages		
	Sand, Continental, Variegated 3	Sand, Coal-bearing Formations 16	Sand, Seacoast, Humid 11	Sand, Basin Average 30	Clay, Basin Average 148			
	Clay 289	Sand 106	Carbonate 116					
La	49	33	35	36	67	61	42	10
Ce	86	60	74	69	130	120	78	20
Pr	12	9	10	9.7	16	15	11	2.5
Nd	39	30	39	34	58	54	38	9
Sm	8	7	8.2	7.6	12	11	8.4	2.1
Eu	--	--	--	--	--	--	--	--
Gd	--	6.2	8.2	7.1	9.5	9.0	7.1	2.7
Tb	--	--	1.5	--	2.7	--	--	--
Dy	--	4.5	6.0	5.2	7.0	6.9	6.9	2.1
Ho	--	--	--	--	2	--	--	--
Er	--	3.5	4.8	4.0	4.6	4.6	4.9	1.7
Tm	--	--	--	--	--	--	--	--
Yb	--	3.1	4.4	3.7	4.4	4.5	4.4	1.6
Lu	--	--	--	--	--	--	--	--
Y	--	37	57	45	53	53	54	23
$\Sigma$ REE	270	190	250	220	370	340	260	70

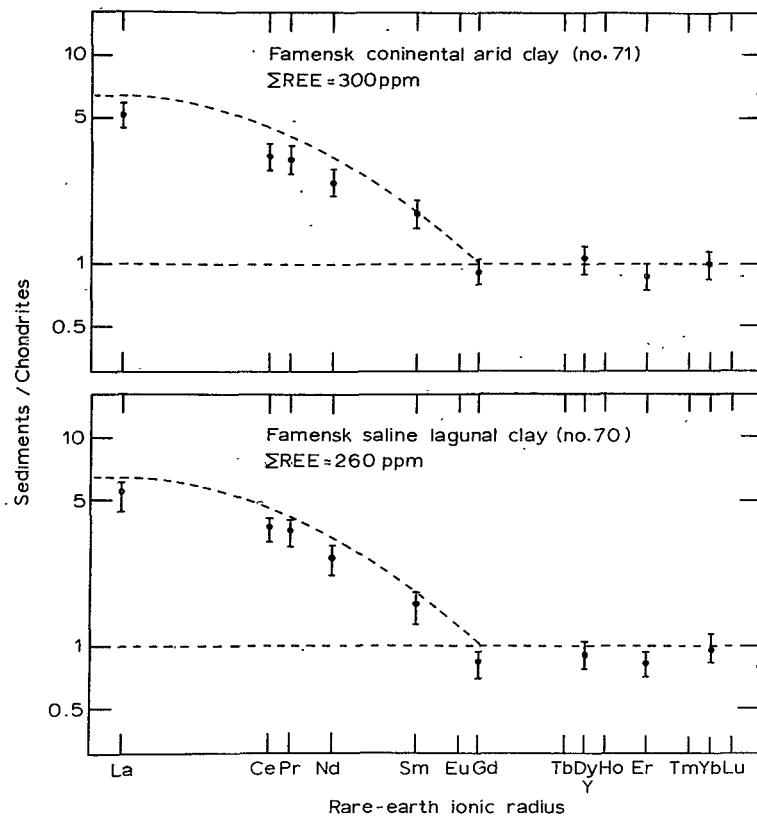


Fig. 42. Comparison plot for Famensk clays (Table 33).

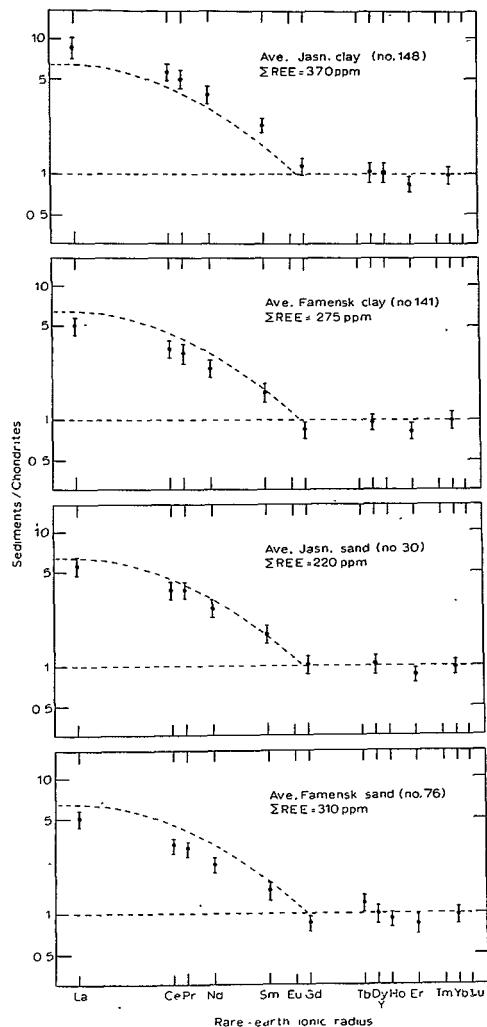


Fig. 43. - Comparison plot for average Famensk and Jasnopoliansk sands and clays (Table 33).

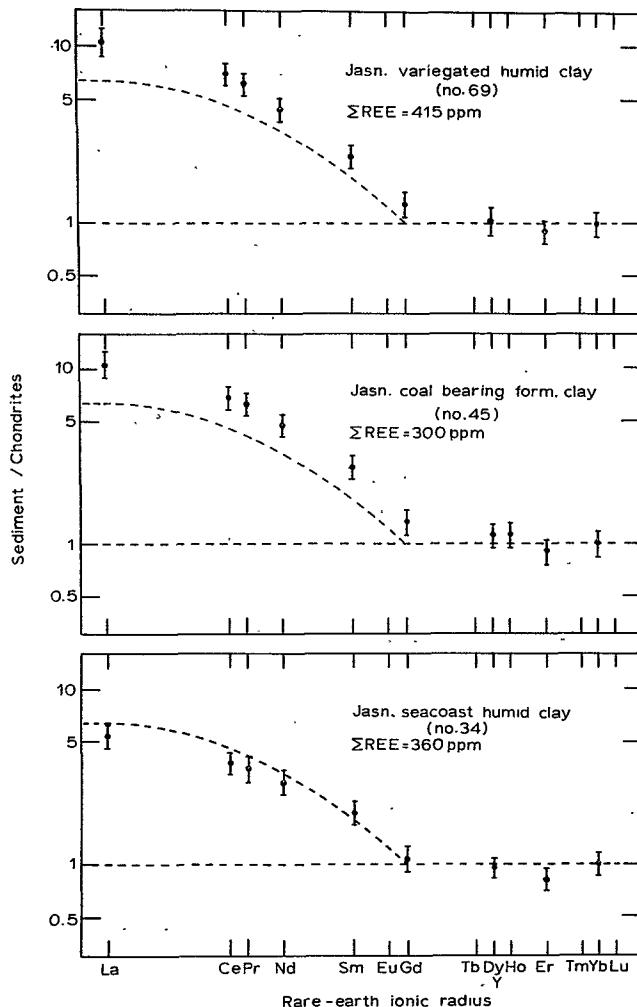


Fig. 44. Comparison plot for Jasnopoliansk clays (Table 33).

contents of the clays increase again in the transition zone to the seacoast facies, and remain high in that facies in the central sectors of the basin. The RE patterns of these clays are shown in Fig. 44. Relative to the continental and coal-bearing clays, the seacoast clays are significantly richer in the heavy REE. Similar trends, but not so marked, were found for the sandstones. The highest carbonate RE contents occurred in the seacoast formations. The carbonates also contained relatively high amounts of the heavy REE.

When the average values for the Jasnopoliansk sediments are considered by rock type rather than by zones of formation, the total RE contents and the relative amounts of light lanthanides decrease in the order clays, sandstones, carbonates. The RE contents of the terrigenous rocks of the Famensk and Jasnopoliansk basins were approximately the same, and this was considered to be a direct confirmation of the common character of their sources of supply.

Average RE contents and patterns for the Russian Platform, according to Balashov, *et al.*, are given in Table 33 and Fig. 45. The total RE contents and the relative amounts of the light lanthanides in the distributions decrease in the order shales, sandstones, and limestones, which is a result of the differentiation of the Jasnopoliansk substage. As mentioned previously, the average sediment RE pattern for the Russian Platform is identical with that of the American shale composite and the average of the patterns for 34 individual sedimentary rocks (Fig. 41).

Balashov, *et al.*, compared the behavior of the REE in the Jasnopoliansk basin with that of the hydrolyzate elements Al, Ga, and Ti. The abundances of these latter elements in the sediments of the Jasnopoliansk basin decrease from the areas of ablation to the central parts. The behavior of the REE is similar, except for the increase in their abundances in the sediments beyond the coal-bearing formations. The maximum RE content occurs in the kaolinized clays of the variegated regions, and this also coincides with the maximum for Al, Ga, and Ti. The simultaneous occurrence of the

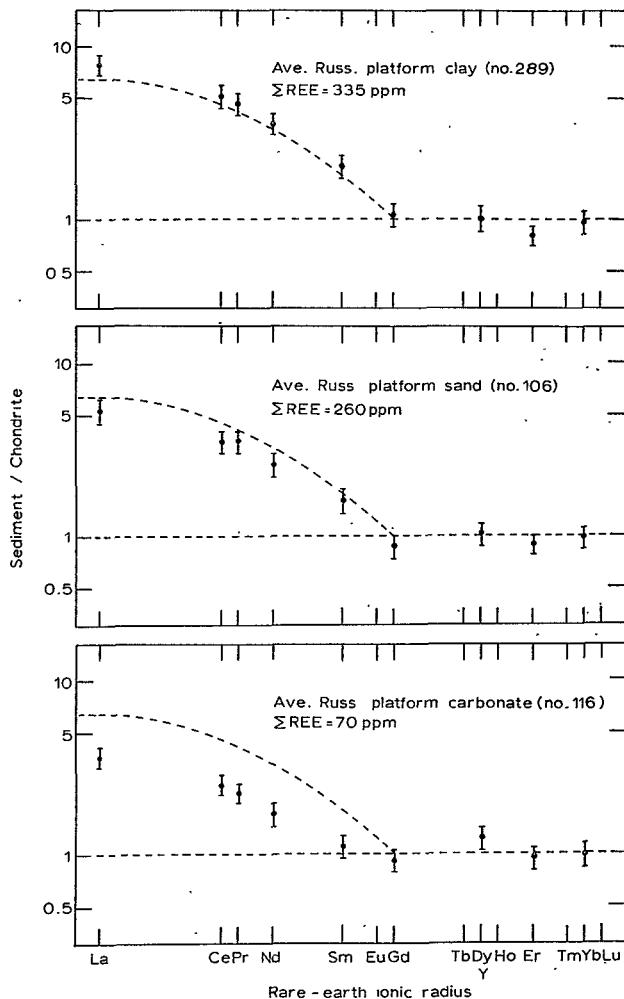


Fig. 45. Comparison plot for average Russian Platform clay, sand, and carbonate (Table 33).

maxima for both of these element groups is reasonable, since under conditions of crustal weathering, hydrolysis of all these elements takes place to produce very slightly soluble substances. These insoluble products are then washed out of the ablation zone and deposited in the adjacent areas. The products of the hydrolysis of the less abundant elements accumulate with those of the more abundant Fe and Al.

The REE deviate in behavior from the hydrolyzates, however, in that their abundances in the sediments undergo an increase deeper in the basin. Balashov, *et al.*, interpret this to be a result of the higher basicities of the REE as compared with the hydrolyzates, which would render them more soluble than the latter in weakly acidic media. In the areas of the coal-bearing formations, where the minimum RE contents were encountered, the products of decomposition of organic matter could have acidified the waters sufficiently to dissolve the REE and perhaps to complex them as well. This leaching, which would not affect the hydrolyzates proper, would account for the low sediment RE contents of that region.

The REE which reached the sea basin from the areas of weathering presumably arrived in two forms, colloidal dispersions or thinly clastic suspensions, and dissolved ionic or complexed species. The main mass of suspended material would be expected to have coagulated and precipitated near the source areas, so the role of the dissolved species would become relatively more important toward the interior of the basin and attain maximum importance in the marine environment. Two samples of marine carbonate were dissolved in 10 per cent HCl, and only 10 and 25 per cent of the total REE remained bound in the insoluble portions. The RE concentrations of the residues were close to those of the clays of the marine and seacoast facies. The high proportions of the REE associated with the carbonate matrix were taken to be evidence of the importance of transport of the REE to the seas as dissolved species. The alkaline conditions of the seas would bring about hydrolysis of the dissolved REE, which would

then tend to adsorb onto colloidal suspensions of clay minerals or organic materials. These would finally be precipitated as a consequence of the high salinity of the sea water. This would account for the appearance of the second maximum in clay RE content in the basin, as opposed to the single maximum for the hydrolyzates Al, Ga, and Ti. Balashov, et al., also suggest that diagenesis may accompany the formation of the sediments to fix the REE as phosphates.

Thus, during the humid Jasnopoliansk substage, the geochemical behavior of the REE approximated that of the hydrolyzates in the marginal, variegated facies of the basin, but approached that of the alkali and alkaline-earth elements in the interior, coal-bearing regions. A parallel increase in the contents of the REE, Mg, Ca, and K was observed in the sediments in the transition from the coal-bearing to the marine facies.

Balashov, et al., suggest that the increased prevalence of the heavier REE, which are actually higher in absolute abundance in the marine than in the continental sediments, is due to the relatively greater ability of these elements to form complexes. They deem it unlikely that the REE could migrate in surface waters as simple ions, since with pH values close to neutral, their hydrolysis would occur. Transport as complexes, possibly with carbonate or bicarbonate, was suggested as a possible alternative. It was also pointed out that the distribution pattern of the REE associated with the HCl soluble portion of the marine carbonates was much richer in the heavy REE than the pattern of the insoluble residue.

Balashov, et al., also comment on some preliminary data on Indian Ocean sediments. Sediments of the northern Indian Ocean, which is fed by waters from a humid, tropical zone, are relatively enriched in the heavy REE. The light REE are more predominant in carbonaceous silts of the central Indian Ocean, adjacent to Australia (an arid region). Sediments from the southern Indian Ocean (Davis sea) are similar in RE patterns to those from the central part. This suggests that ice ablation does not offer much opportunity for extensive mineral decomposition or chemical change.

Average RE contents for clays, sands, and carbonates are given by Balashov, et al., as 335, 260, and 70 ppm, respectively. They give 275 ppm as the average for all sedimentary rocks.

#### PHOSPHATIC MATERIALS

The geochemical association of the REE with phosphate in both igneous and sedimentary materials has long been recognized and is clearly illustrated in the RE contents of phosphorites and phosphatic fish remains, for which numerous analyses are available.

ARRHENIUS, BRAMLETTE, and PICCIOTTO (1957) gave evidence for the removal of the REE from sea water by surface adsorption onto microcrystalline fishbone apatite. The REE were presumed to replace Ca on the surface and thus to form highly insoluble phosphates, and possibly fluorides. This replacement was found to take place only in deep water, where the apatite is in a state of slow dissolution. Shallow water bone apatite was not found to accumulate significant quantities of the REE.

ARRHENIUS and BONATTI (1964) reported studies of pelagic fish bone apatite which appeared to have very unusual RE patterns as compared with sediments and ocean water. In particular, Nd was found to be much more abundant than Ce or La and was matched in abundance only by Y. Relative to the other heavy REE, Yb was found to be enriched by an order of magnitude. These patterns were taken by the authors to be evidence of the authigenic formation of the apatite. It is difficult to conceive of a plausible mechanism for producing such patterns, and no similar systematic irregularities have been reported by other investigators, so the possibility of analytical error in the results cannot be overlooked.

KOCHENOV and ZONOEV'EV (1960) studied the RE distributions and contents in fish bone detritus from various Mesozoic and Cenozoic sediments of the USSR. The fossils examined came from quite varied lithologic surroundings. Some deposits had been laid down in bottom waters poisoned

by hydrogen sulfide. Others were in silty, glauconitic clays and carbonate rocks. The fish remains varied greatly in size, form, structure, and chemical and mineralogical composition. The principal constituent of the fossils was carbonated fluoroapatite. Up to 5 per cent organic matter was also found.

The gross compositions of the bone fossil materials were compared with those of modern fish. The fossilization processes had scarcely altered the  $P_2O_5$ ,  $SrO$ ,  $K_2O$ ,  $Na_2O$ ,  $SO_2$ , and  $Cl^-$  contents, but had decreased the  $CO_2$  contents greatly and had increased the  $F^-$  contents about 10 times.

A linear relationship was found between the total RE and  $P_2O_5$  contents of the materials, over the entire range of  $P_2O_5$  (0.4 to 9 per cent) and REE (<0.01 to 0.4 per cent) encountered. The average total REE/ $P_2O_5$  ratio was 0.03, and the ratio never exceeded 0.053. The RE contents and the REE/ $P_2O_5$  ratios decreased from small bone fragments to large ones. Solid, massive bones, teeth, etc., had the lowest RE contents and REE/ $P_2O_5$  ratios as low as 0.003. Low REE/ $P_2O_5$  ratios were also found in materials whose pores were filled with calcite, celestite, or barite. These minerals presumably isolated the bones from the surrounding medium and prevented further contact with REE. Bone surfaces were relatively enriched in REE, while the interiors were decidedly lower. Bones from mammals, reptiles, and birds had the same RE contents as fish bones.

Kochenov and Zonov'ev stated that the high absolute RE content in phosphatic remains involves diadochic substitution of  $Na^+ + REE^{+++}$  for  $Ca^{++}$ . In terms of distribution patterns, a relatively high Y content was localized in sulfide layers with low  $CO_3^-$  and high organic contents, i. e., those layers characteristic of relatively deep water deposits. There is considerable variation among the individual RE patterns, but the average distribution for all the phosphatic detritus (Table 34, Fig. 46) is very similar to that found in common sediments, except for Eu, which is quite low.

Analyses of the remains of Paleozoic fish from the Russian Platform were made by BLOKH (1961). These remains were found usually to contain

Table 34. RE Contents of Some Phosphatic Materials (ppm)

	Mesozoic and Cenozoic Fish Bone Detritus <sup>a</sup> (Avg.)	Paleozoic Fish Remains <sup>b</sup> (Avg.) <sup>c</sup>	Phosphorites, Russian Platform <sup>d</sup> (Avg.) <sup>c</sup>	Phosphorite, California <sup>e</sup>	Phosphorite, Phosphoria Formation <sup>f</sup>
La	1,500	23.	16.	56	160
Ce	2,700	47.	32.	103	-----
Pr	500	11.2	7.0	14.4	34
Nd	1,500	36.	23.	58	96
Sm	430	9.5	5.2	11.2	24
Eu	20	-----	0.7	2.8	5.8
Gd	330	9.8	5.8	15	-----
Tb	30	1.24	0.8	2.2	3.5
Dy	300	6.4	3.7	12.6	-----
Ho	50	1.15	0.8	3.3	3.9
Er	220	2.5	2.3	9.1	-----
Tm	-----	-----	0.3	1.08	2.1
Yb	100	1.0	2.5	7.0	11
Lu	-----	-----	0.4	1.16	-----
Y	1,750	28.	-----	140	200
$\Sigma$ REE	1,000- 13,400	1,100- 16,500	260- 3,100	440	910

<sup>a</sup>KOCHENOV and ZONOV'EV (1960).<sup>b</sup>BLOKH (1961).<sup>c</sup>Relative, not absolute, values.<sup>d</sup>SEMENOV, KHOLODOV, and BARINSKII (1962).<sup>e</sup>GOLDBERG, et al. (1963).<sup>f</sup>SCHOFIELD and HASKIN (1964).

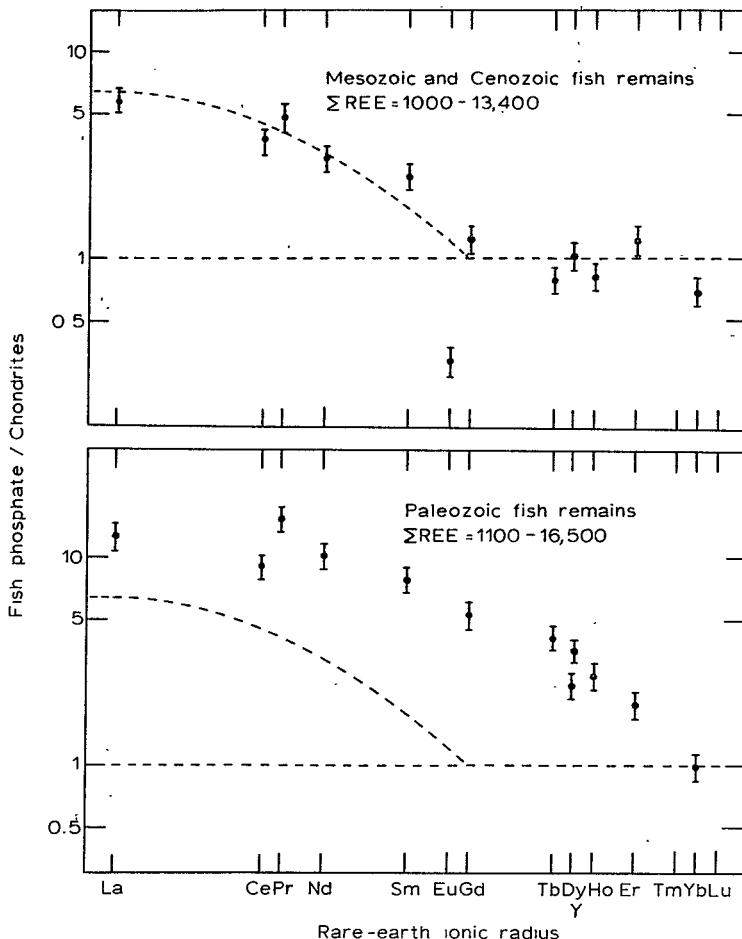


Fig. 46. Comparison plot for phosphatic fish remains (Table 34).  
Upper dashed curve represents the North American composite shale.

more than 0.1 per cent REE, the highest content encountered being 4.7 per cent. The highest RE contents were found in fish detritus in sands and clays; bones taken from marlstones usually had much lower REE contents. No regular variation of RE content with depth of burial was apparent. No locality could be characterized by a single value for total RE content. Weathered fossil bones appeared not to have suffered any obvious change in RE content. No correlation was found between RE content and extent of crystallization of the phosphate minerals fluorapatite and francolite.

In only one sample were the heavy REE predominant. One sample contained more La than Ce. Nd was often more abundant than La, but never more abundant than Ce. The average RE content for the Paleozoic fish remains appears in Table 34 and Fig. 46.

The bones of modern fish are not rich in REE, containing at most a few hundredths of a per cent. The redox environments of the enclosing rocks did not seem to affect the RE contents of the fish remains.

Phosphorites contain hundredths to tenths of a per cent REE, but have similar gross compositions. Blokh concluded that if the RE intake were epigenetic, the above facts would not be as they are. Rather, he believed that the REE were taken in during diagenesis, when the bone phosphate took up F<sup>-</sup> and became converted from hydroxyapatite to fluorapatite. The phosphates of the phosphorite beds examined were not subjected to such changes, and this, he presumed, is responsible for their lower RE contents. He further suggested that the absolute RE contents depended on the supply of REE in the bottom waters, where the fish fauna were buried. The RE contents of these waters would depend on the richness of the provenance area and the distance out in the sea. Thus, Blokh concluded that fossil bones buried in fresh water basins are in a more favorable environment to take up REE than are marine organisms. Higher RE contents were, in fact, observed in the samples of continental deposition character rather than in those of marine origin.

The considerable differences in average RE patterns between the Mesozoic and Cenozoic fish detritus examined by Kochenov and Zonov'ev and the Paleozoic fish remains studied by Blokh are interesting, but are not easily explained. Considerable variations among the individual patterns were observed, so the summing of all the patterns of each group might not yield a good statistical average. An average of 67 complete RE analyses on samples from eight locations was given by Kochenov and Zonov'ev, and only 12 analyses were given by Blokh. Blokh suggested that the different patterns observed in the various specimens may reflect different patterns in the sources of supply. However, ten samples of sedimentary rock randomly selected and analyzed would not be expected to yield an average RE distribution as different from the crustal pattern as the average for the phosphorites analyzed by Blokh, so the processes responsible for RE uptake must control the RE patterns to some extent.

SEMENOV, KHOLODOV, and BARINSKII (1962) reported analyses of phosphorites, mostly from the Russian Platform. Fifty-three samples from several geographic regions ranged in total RE content from 350 to 8500 ppm, with an average of 700 ppm. The average RE contents for 23 samples in which the individual REE were analyzed are included in Table 34, and the corresponding RE pattern is shown in Fig. 47. The pattern appears to be less rich in the light REE than is the average pattern for sedimentary rocks. Eu is definitely low relative to its neighboring elements. Most of the individual phosphorite samples had RE patterns very similar to the average, but cases in which the most abundant element was La, Nd, Gd, or Dy were encountered. The RE patterns could not be related to the geologic occurrence or petrography of the phosphorites. Considerable pattern variation was found within single deposits. Older (Paleozoic) phosphorites tended to deviate more from the average than did the younger ones. This is interesting in view of the fact that the average RE pattern for Paleozoic fish bone detritus (BLOKH, 1961) differed from the average for sediments, whereas the younger (Mesozoic

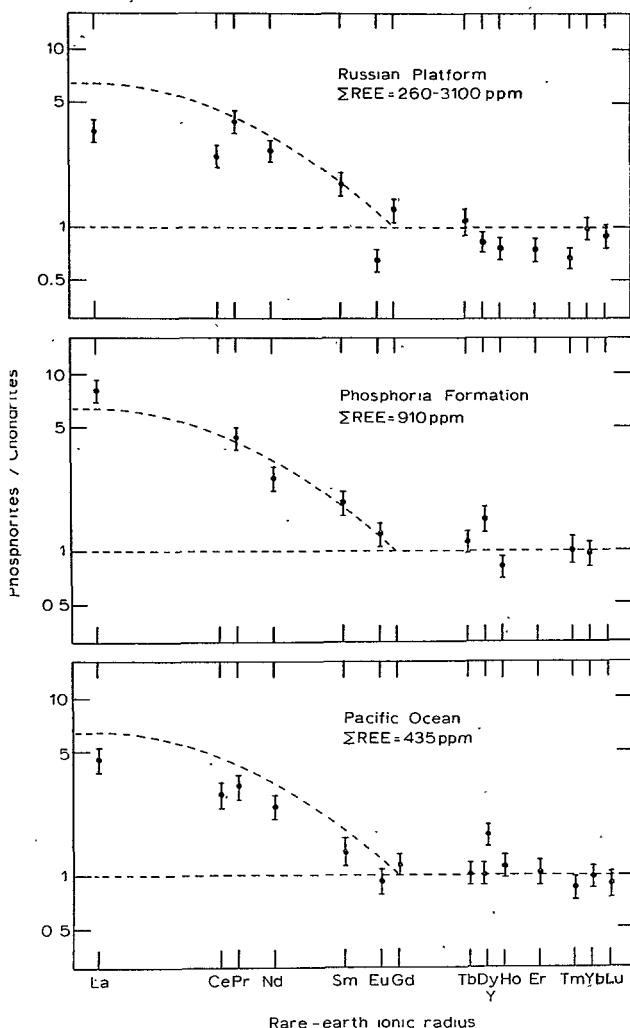


Fig. 47. Comparison plot for phosphorites (Table 34).

and Cenozoic) fish bone remains (KOCHENOV and ZONOV'EV, 1960) yielded the same pattern as sediments, except for Eu. No satisfactory rationalization for the differences among the RE patterns in these materials has yet been proposed.

A single phosphorite dredged from the Pacific Ocean was examined by GOLDBERG, *et al.* (1963). It is believed to have been deposited from sea water. The RE pattern is similar to the average for sediments, except that the light REE are about 25 per cent too low (Fig. 47, Table 34). This is the same trend as was observed by Semenov, *et al.*, for the Russian Platform phosphorites. No significant Eu depletion was found in the Pacific Ocean specimen. A single sample of phosphorite from the Phosphoria formation was analyzed for REE by SCHOFIELD and HASKIN (1964). The distribution pattern was very similar to the average for common sediments (Fig. 47, Table 34). Again, no Eu anomaly was encountered. The REE were enriched relative to Ca in the phosphorite by more than  $10^4$  times as compared with the relative amounts of these elements in sea water.

#### MARINE MATERIALS; OCEAN AND GROUND WATER

The RE content and pattern of ocean water obtained off the southern California coast were measured by GOLDBERG, *et al.* (1963). The values for surface ocean water are listed in Table 35, and the RE distribution pattern is shown in Fig. 48. The absolute RE concentration at a depth of 4000 meters was about four times that of the surface ocean water.

Recently, HAYES, SLOWEY, and HOOD (1965), also using neutron activation analysis, have found the concentration of individual REE in surface water from an offshore station in the Gulf of Mexico to be of the order of  $10^{-6}$  ppm, in agreement with the values obtained for Pacific sea water by GOLDBERG, *et al.* (1963). The work of Hayes, *et al.*, also indicated that approximately half of the REE was present in particulate matter retained on 0.45  $\mu$ -millipore filters by sea water filtration. In Table 36, the contents of eight REE determined by HAYES, HOOD, and SLOWEY (1964) in the soluble and particulate phases of Gulf of Mexico surface water are given. Ratios of RE contents in particulate (that retained by a 0.045- $\mu$ -millipore filter) phase to contents in soluble phase ranged from 0.3 (Pr) to 8.2 (Lu).

Table 35. RE Contents of Marine Specimens (ppm)

	Pacific Ocean Water <sup>a</sup> ( $\times 10^6$ )	Manganese Nodule <sup>a</sup>	Pleistocene Coral <sup>b</sup>	Recent Coral <sup>b</sup>	Modern Sea Shells <sup>b</sup>
La	2.9	11,500	0.052	0.08	0.13
Ce	1.28	52,000	--	2.7	0.78
Pr	0.64	3,600	0.028	--	0.053
Nd	2.3	13,800	--	0.71	0.26
Sm	0.44	6,400	0.013	0.079	0.038
Eu	0.113	1,040	0.0034	0.058	0.012
Gd	0.61	4,600	0.013	0.072	0.055
Tb	--	690	--	0.0058	0.010
Dy	0.73	3,000	--	--	--
Ho	0.22	580	0.006	0.0048	0.010
Er	0.61	1,380	--	0.019	0.036
Tm	0.13	170	--	0.0032	0.0005
Yb	0.52	460	0.0084	0.018	0.019
Lu	0.116	115	--	--	0.003
Y	--	--	0.099	0.124	0.22
$\Sigma$ REE	$16 \times 10^{-6}$	99,000	0.4	4	1.7

<sup>a</sup>GOLDBERG, et al. (1963).<sup>b</sup>SCHOFIELD and HASKIN (1964).

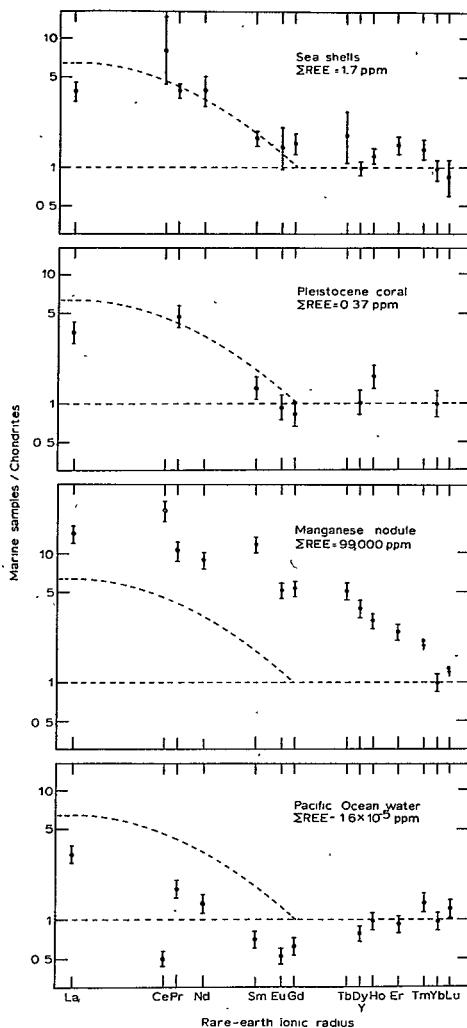


Fig. 48. Comparison plot for marine materials (Table 35).

Table 36. RE Contents in Gulf of Mexico Surface Water  
 $(\times 10^6)$  (ppm)<sup>a</sup>

	Particulate Phase	Soluble Phase	Total	Ratio $\frac{\text{Gulf of Mexico}}{\text{Pacific Ocean}} \text{ Water}$
Ce	26	---	26	20
Pr	1.1	3.1	13.1	21
Sm	9.1	2.2	11.3	26
Eu	2.4	0.4	2.8	25
Dy	7.2	5.3	12.5	17
Ho	(15) <sup>b</sup>	1.5	(16) <sup>b</sup>	(73) <sup>c</sup>
Yb	2.4	2.7	5.1	10
Lu	4.1	0.5	4.6	40

<sup>a</sup>HAYES, HOOD, and SLOWEY (1964).

<sup>b</sup>Possibly in error owing to equipment malfunction.

<sup>c</sup>A very doubtful ratio; see (b) above.

For seven of the elements given (Ce, Pr, Sm, Eu, Dy, Yb, and Lu--Ho is excluded, see Table 36), the average ratio of REE in Gulf of Mexico surface water to REE in Pacific Ocean water is  $23 \pm 7$ . Since the Ce ratio of 20 in the two waters agrees well with the average of  $23 \pm 7$ , it is concluded that Hayes, Hood, and Slowey have confirmed the observation by Goldberg, et al., that Ce has been depleted relative to the other REE by a factor of about six, at least for waters surrounding the western hemisphere. The above depletion factor assumes that the average relative RE pattern initially distributed in sea water approximates the RE pattern in sediments.

Whether the soluble fraction of the REE are present as ionic or complex species in sea water or on particulates smaller than  $0.45 \mu$  remains an open question. For a summary of the present state of knowledge concerning REE in sea water, the reader is referred to a very recent report by HØGDAHL (1965) and a dissertation by SPIRN (1965).

The REE in the ocean are presumably derived from crustal rocks, but the oceanic abundance pattern certainly differs substantially from the crustal average. The depletion of Ce may be due to its oxidation and incorporation into Mn nodules, as described below. The relatively high concentrations of the heavy REE were attributed to the greater stability of soluble complexes for these elements, or to a differential adsorption onto solid surfaces.

By presuming an influx of  $2 \times 10^{15}$  g of solid material into the oceans every year with an average RE content and pattern as given by RANKAMA and SAHAMA (1950), Goldberg, et al., calculated oceanic residence times for the lanthanides, as defined by the relation  $t_A = A/(dA/dt)$ . In this equation, A is the total amount of an element present in the oceans, and  $dA/dt$  is the amount of that element introduced into or precipitated from the ocean per unit time, assuming steady state conditions. The residence times ranged from 80 yr for Ce to 1800 yr for Tm. WILDEMAN and HASKIN (1965) repeated the calculations, using a more accurate estimate of the RE content of weathering crustal material, and obtained the shorter residence times which are given in Table 37. Wildeman and Haskin also showed that the difference in RE pattern between the ocean and sedimentary rocks did not

Table 37. Residence Times for REE in Ocean Water<sup>a</sup>

	Residence Times (yr)
La	210
Ce	48
Pr	180
Nd	180
Sm	180
Eu	160
Gd	280
Ho	440
Er	430
Tm	630
Yb	390
Lu	570

<sup>a</sup> WILDEMAN and HASKIN (1965).

indicate absence of equilibrium between these two phases. The entire oceanic RE content is the same as the amount found in the top  $\sim 0.05$  g of sediment per  $\text{cm}^2$  (or  $\sim 0.2$  mm thickness) of ocean floor. Hence, the extraction of all the REE in the ocean from the material passing through it would not alter the RE pattern in that material sufficiently to be detectable.

BALASHOV and KHITROV (1961) studied the REE as a group in sea water from numerous stations in the Indian Ocean. The surface water concentrations ranged from 0.25 to  $1.2 \times 10^{-3}$  ppm. A gradual increase with depth all the way to the bottom was confirmed by measurements at two stations. The increase in concentration with depth is similar to that found by Goldberg, et al., but the absolute RE content of  $\sim 10^{-3}$  ppm is much higher than the  $\sim 10^{-5}$  ppm value of Goldberg, et al. However, it does correspond to the value of  $\sim 10^{-3}$  ppm listed by GOLDSCHMIDT (1954). Perhaps the enhancement of RE content by  $\sim 10^2$  in the Indian Ocean compared with the eastern Pacific Ocean may be attributed to increased leaching of the large monazite areas in the Indian area. At such low levels of RE content, contamination problems in analyses become quite severe. More RE analyses of sea water from various depths and locations will explain the real, or apparent, discrepancy.

Balashov and Khitrov also attempted to determine the chemical forms of the REE in ocean water. Suspended material with a diameter of  $7\ \mu$  or greater was filtered out and analyzed. The RE contents of the material filtered out were high, ranging from 350 to 1400 ppm, but accounted for less than 50 per cent of the REE in the volume of water filtered. Investigations of the RE contents of plankton were undertaken. From 60 to 420 ppm REE (based on dry weight) were found, but this accounted for only a fraction of a per cent of the REE in the water from which the plankton were extracted. Calculations indicated that the REE were not present as insoluble hydroxides, because the RE content of ocean water is too low to precipitate even such insoluble compounds. It was concluded that the REE, in addition to the portion associated with filterable suspensions, were probably present to some extent as dispersed ions, as colloids, and as complex species.

It was shown that although the concentration of matter suspended in

water does not increase with depth, the RE content of the suspended matter does. Therefore, it appears that the suspended particles adsorb the REE from sea water during their descent.

A relatively higher RE content for near-shore waters was taken to indicate a terrigenous source for most of the REE found in the ocean. In order to estimate the possible contribution from wind-borne matter, dust collected by airplane over the northern Indian Ocean was analyzed. The mineral component of the airborne material yielded 90 to 170 ppm REE, which corresponds to about  $10^{-3}$   $\mu\text{g}$  of REE per cubic meter of air. The mineral fraction thus has about the same RE content as terrestrial rocks and the suspended surface matter in the ocean.

ROBINSON, BASTRON, and MURATA (1958) determined the REE in ground waters from two wells west of Washington, D. C. The absolute RE contents were 2 and  $60 \times 10^{-3}$  ppm, which is similar to the contents in Indian Ocean water described above. The individual RE contents are given in Table 38. The distribution pattern of the well for which the most data are given is strongly dominated by the heavy REE, with Y contributing more than two-thirds of the total and Yb being the most abundant lanthanide.

SCHOFIELD and HASKIN (1964) analyzed two corals and a composite of modern sea shells for REE. The RE contents of these materials are very low (0.4 to 4 ppm) (Table 35), considerably lower than the RE contents of limestones. The REE were enriched relative to Ca by a few hundred times as compared with sea water. The RE patterns are more similar to the average for common sediments than to that of ocean water (Fig. 48).

A manganese nodule from the Pacific Ocean was found by GOLDBERG, et al. (1963), to have a high RE content of 99,000 ppm and a RE pattern very different from those of sedimentary rocks and the ocean water which presumably served as its source (Fig. 48, Table 35). In particular, the pattern showed considerable fractionation of the heavy REE and an anomalously high Ce abundance. The Ce was presumed to have been oxidized to the +4 state and then incorporated into the nodule as  $\text{CeO}_2$ , along with  $\text{MnO}_2$  (GOLDBERG, 1961). The incorporation of Ce into Mn nodules by such a process might account for its relative depletion from ocean water (see above).

Table 38. RE Contents of Water From Two Wells  
Near Washington, D. C. (ppb)<sup>a</sup>

	Clifton	Falls Church
La	12	0. 4
Ce	0. 5	-----
Nd	0. 7	-----
Dy	0. 7	-----
Er	0. 8	-----
Tm	0. 3	-----
Yb	1. 6	0. 03
Lu	0. 3	-----
Y	41	0. 8

<sup>a</sup> ROBINSON, BASTRON, and  
MURATA (1958).

The RE pattern of the Mn nodule shows a noticeable enrichment of Sm relative to its neighbors. Goldberg, et al., suggested that this may be due to the similarity in ionic radius between Sm and Cu, which also tends to concentrate in Mn nodules (GOLDBERG, 1954). Analytical error or statistical anomaly seems a more plausible explanation, however, because the stringent dependence of substitution on ionic radius cannot be justified.

#### COAL

The first extensive studies of REE in coals were made by GOLDSCHMIDT and PETERS (1933) as part of a general investigation of trace elements in coal ash. They found an average of 100 ppm Y and a maximum of 800 ppm Y in the ash of a number of West German and British coals. Since the average value considerably exceeds the Y content to be expected if the ash were detrital mineral matter, Goldschmidt and Peters concluded that inorganic processes alone were insufficient to account for the REE in coal ash and that some mode of biologic accumulation had occurred.

YERSHOV (1961) reported values for the RE content of coal ash from the Kizelovskii coal basin. The material examined is believed to have accumulated from organic matter in an extensive river delta during the Carboniferous period. The contents of most of the trace elements (Ga, Cu, Pb, Co, Ni, V, Cr, Mn, Ti) studied in coals of this region were found to be independent of the petrography of the coal, but to correlate well with the amount of detrital material in the coal ash. Ge and Be abundances were found to depend on the organic content of the coal.

The RE distribution in the Kizelovskii coal (Table 39, Fig. 49) shows considerable deviation from that which might be expected if the presence of the REE were solely due to detrital material. A selective accumulation of the heavy lanthanides and Y has occurred. Also, Yershov showed that the Y and Yb are associated predominantly with the organic

Table 39. RE Contents of Coals (ppm)

	Kizelovskii <sup>a, b</sup>	Pennsylvania <sup>c</sup>	Illinois <sup>c</sup>	Chekez <sup>b, d</sup>
La	6.0	4.9	3.3	26
Ce	18	12.2	10.8	4.9
Pr	2.6	1.8	2.6	8.6
Nd	8.0	3.6	5.8	21
Sm	2.3	1.22	2.0	5.8
Eu	0.1	0.52	0.81	----
Gd	1.9	1.22	1.9	4.9
Tb	0.35	0.22	0.36	----
Dy	2.5	---	---	3.7
Ho	0.7	0.19	0.42	----
Er	2.0	0.50	0.73	1.8
Tm	0.4	0.06	0.13	----
Yb	2.2	0.37	0.57	1.6
Lu	---	---	0.072	----
Y	53	4.0	5.3	21
$\Sigma$ REE	---	32	36	----

<sup>a</sup> YERSHOV (1961).<sup>b</sup> Relative, not absolute, values.<sup>c</sup> SCHOFIELD and HASKIN (1964).<sup>d</sup> KOSTERIN, KOROLEV, and KIZYURA (1963).

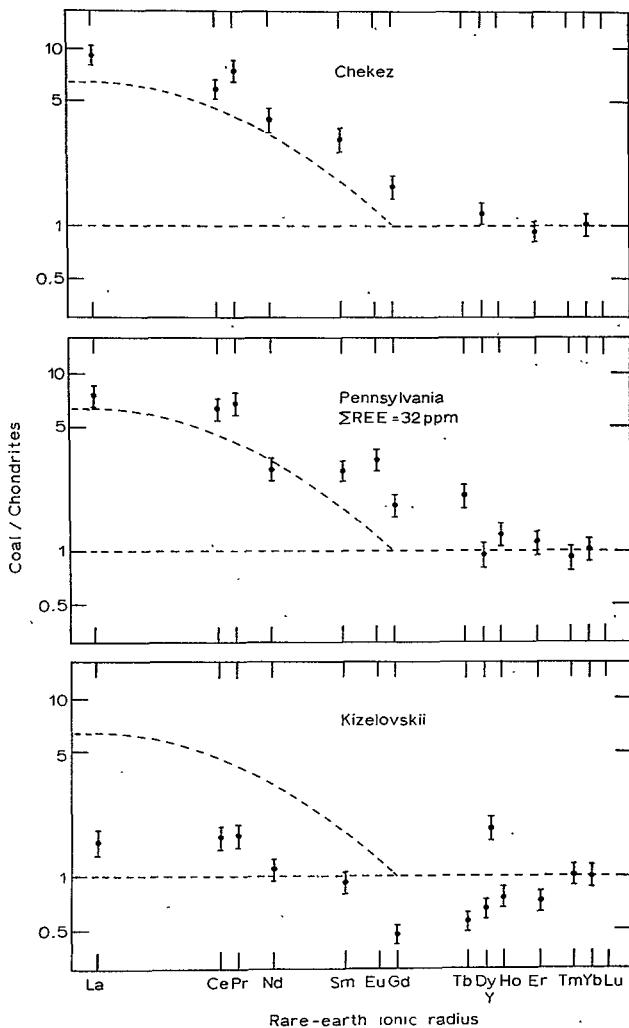


Fig. 49. Comparison plot for coals (Table 39).

matter in the coal. He thus attributes the RE pattern to a selective capture of the heavy REE by organic matter. Certainly, the distribution shown in Fig. 49 could occur by a combination of such selective capture of the heavy REE plus detrital material with a normal crustal RE pattern.

SCHOFIELD and HASKIN (1964) determined the RE contents and distributions in two samples of coal from southern Illinois and western Pennsylvania (Table 39, Fig. 49). The RE contents and patterns of these two samples are very similar. Compared with sedimentary rocks, they are relatively richer in the elements Sm-Ho, and especially in Eu. The ash contents of the coals were 6.0 and 7.5 per cent. This corresponds to a La content in the ash of 50 to 100 ppm, which was considered to be too high to correspond to a purely detrital origin for the REE.

On the other hand, Schofield and Haskin estimated that the total quantity of REE in the live plants which eventually gave rise to the coal could well have been greater than that now present in the coal. They suggested that during the deposition of the coal under reducing conditions, part of the REE in the plants were leached away, but Eu was more nearly quantitatively retained by some mechanism involving its reduction to the +2 state. Selective leaching of the lightest REE in a weakly acidic environment plus simultaneous selective removal of the heaviest REE by organic complexing agents was deemed necessary, provided that the RE pattern in the plants was the same as the crustal average.

KOSTERIN, KOROLEV, and KIZYURA (1963) examined a coal from the Chekez lignite deposit. The coal had a high pitch content, and the ash contained abundant mineral impurities, especially feldspar, quartz, fragments of extrusive rocks and shales, and iron sulfides. The coal is believed to have been laid down under reducing conditions varying from weakly acid to weakly basic. Metamorphic and placer monazite were found nearby.

The RE content and pattern of this coal are given in Table 39 and Fig. 49. The most striking feature of the distribution pattern is the

extreme Ce deficiency. Kosterin, et al., attribute this to some mechanism involving the oxidization of Ce to the +4 state. Certainly, this is plausible if the REE found in the coal are of biogenic origin, since ROBINSON, BASTRON, and MURATA (1958) found that for certain soils, it was not possible for plants to extract Ce in quantities comparable to the other REE, owing to its oxidation and fixation as highly insoluble  $\text{CeO}_2$ .

Kosterin, et al., also cited an anomalously low content of Eu, and attributed this to its reduction in the reducing environment of coal formation and its removal from the rest of the REE.

It is interesting to note from Fig. 49 the considerable variation in the RE patterns for the coals. It is also interesting that reduction of Eu to the +2 state was invoked to explain the relative enrichment of that element in one coal and its absence from another. It must be concluded that aside from the probable biogenic origin of much of the REE in these coals, little is understood about the origin of the RE patterns.

#### SOIL

A summary of qualitative and semiquantitative observations of the REE in soils is given by VINOGRADOV (1959). The variability in total RE content is similar to that found for igneous rocks and shales. Vinogradov also lists values for the individual REE in six Russian soils. The highest total RE content was 200 ppm for a mountain tundra soil, and the lowest was 6 ppm in the B horizon of a soil derived from basic rock. The average of the six Russian soils is included in Table 40. The RE pattern is essentially the same as the average for sediments.

ROBINSON (1914) found from 100 to 800 ppm REE in a number of soils from the United States. The exchangeable REE in three soils and a soil clay were analyzed by ROBINSON, BASTRON, and MURATA (1958) in connection with their studies of RE uptake by hickory trees. The average of the relative amounts of the individual REE in these four samples are included in Table 40 and are shown in Fig. 50. A further discussion of REE in these soils is included later in the section on REE in plants.

Table 40. RE Contents of Biologic Materials (ppm)

	Cattle Bone Ash <sup>a</sup>	Animal Bone <sup>b</sup>	Mouse Ash <sup>c</sup>	Soil Extract <sup>d, e</sup>	Hickory Leaves <sup>d, e</sup>	Opium Ash <sup>f</sup> (Avg.)	Singapore Opium Ash <sup>f</sup>	Russian Soil <sup>g</sup>
La	0.0024	0.27	0.33	16	16	4.3	2.7	29
Ce	0.0044	--	0.58	24	14	34	12	56
Pr	--	--	0.073	2.5	1.8	1.5	0.68	7.0
Nd	0.0022	--	0.33	19	20	18	7.8	27
Sm	0.0004	0.009	0.043	2.5	1.4	1.6	1.3	6.5
Eu	--	0.20	0.016	0.8	0.8	0.32	0.13	0.6
Gd	0.0010	0	0.049	3.0	3.1	--	--	4.3
Tb	--	0.0004	0.012	0.7	0.6	0.26	0.32	0.6
Dy	0.0008	0.00	--	2.8	2.4	0.62	0.34	2.5
Ho	--	0.50	0.017	0.7	0.7	0.19	0.081	0.6
Er	0.0002	2.2	0.035	1.5	2.4	2.2	1.0	0.6
Tm	--	1.30	0.010	0.22	0.2	0.40	0.14	0.6
Yb	--	1.30	0.026	0.9	1.1	0.58	0.46	0.6
Lu	--	0.08	0.0075	0.1	0.2	0.02	0.005	0.6
Y	--	0.04	0.24	25	36	4.8	3.6	--
$\Sigma$ REE	--	--	1.8	--	--	69	31	--

<sup>a</sup>LUX (1938).<sup>b</sup>BROOKSBANK and LEDDICOTTE (1953).<sup>c</sup>POETZ and HASKIN (1966).<sup>d</sup>Relative, not absolute, values.<sup>e</sup>ROBINSON, BASTRON, and MURATA (1958).<sup>f</sup>PAPPAS, ALSTAD, and LUNDE (1963).<sup>g</sup>VINOGRADOV (1959).

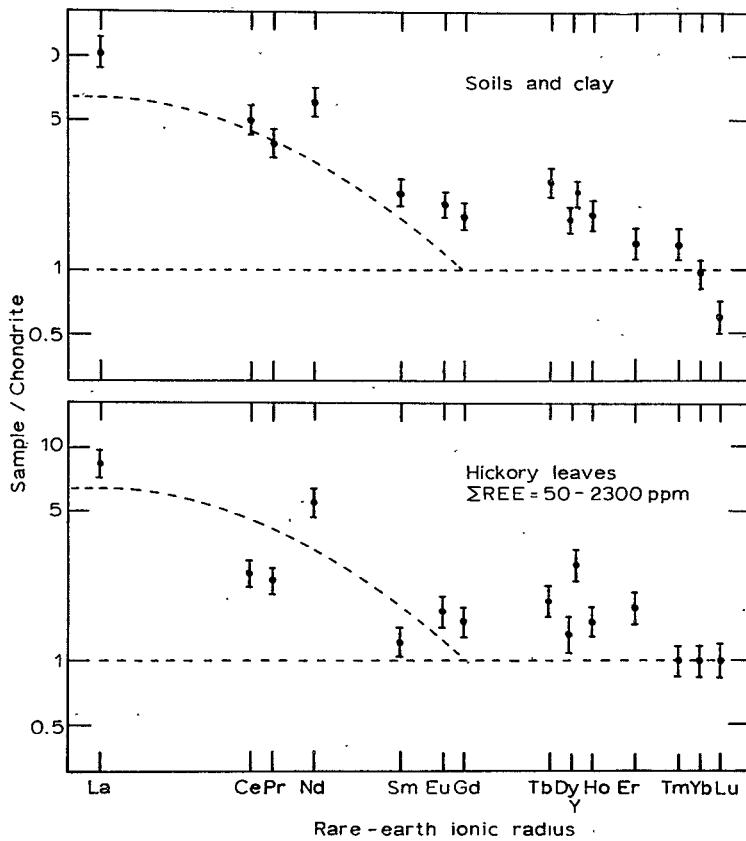


Fig. 50. Comparison plot for hickory leaves and soils on which they were grown.

BIOSPHERE

There have been numerous qualitative and some semiquantitative reports in the literature of the occurrence of various members of the RE group in a wide variety of biologic materials. From these reports, no more can be safely concluded than that very small amounts of the REE are found in living matter. A few careful investigations have been made of RE contents and distributions in biologic organisms, and these are summarized below.

LUX (1938) achieved a successful quantitative determination of several of the REE in bone tissue by ashing 6 kg of cattle bones to obtain 2.2 kg of ash. The ash was dissolved in 3.4 liters of conc. HCl. Macroscopic amounts of Pr and Tm were added as a "tracer," and after painstaking chemical work, a 35 per cent yield for the separation of the RE group was attained. The analytical results are given in Table 40.

The principal reason for undertaking the project was to determine whether the REE might become concentrated in the hydroxy-apatite mineral of bones, as the high RE contents of inorganic apatites had recently been established. The low RE content of the bone ash ( $\sim 10^{-3}$  ppm) led Lux to conclude that the mammalian system discriminates against the REE relative to Ca. The relative RE distribution pattern of the bone ash is remarkably similar to the crustal average, but Gd and Dy are sufficiently enriched that selective biologic discrimination was possibly observed.

In a paper devoted mostly to a discussion of activation analysis for the REE, BROOKSBANK and LEDDICOTTE (1953) reported RE concentrations found in a sample of animal bone. These values appear in Table 40. The absolute concentrations are higher than those described by LUX (1938) and by POETZ and HASKIN (1966), and the relative RE pattern shows considerable random scatter. Thus, it is probable that some of these values may be in error. The heavy REE do predominate the distribution, so strong biologic fractionation might have occurred.

POETZ and HASKIN (1966) determined the RE content of a laboratory mouse. The absolute abundances are included in Table 40, and the relative RE distribution is given in Fig. 51. The relative abundances of the light REE are the same as for the crustal average. There is sufficient scatter among the points for the heavy REE to prevent biologic fractionation from being ruled out. The heavy REE may have been relatively enriched as a group.

It is not possible to say whether true biologic fractionation has occurred in any of the above specimens, first, because the relative distributions of the various chemical forms of the REE taken in are not known and, second, because the data are too few and not sufficiently accurate. However, there is indication of a possibly slight relative enrichment of the heavy REE as compared with the light REE in all three samples. This conclusion is further supported by the results of ROBINSON, BASTRON, and MURATA (1958), for hickory leaves.

ROBINSON, WHETSTONE, and SCRIBNER (1938) discovered remarkably high RE contents, as much as 2000 ppm (dry weight basis), in hickory leaves. ROBINSON (1943) surveyed the total RE contents of a number of crop plants and of hickory leaves and determined the amounts of extractable REE from several soils. The total RE contents of the crop plants appear in Table 41. The RE contents of hickory leaves varied from 3 to 2300 ppm of their dry weight. An attempt was made to correlate the RE contents of the hickory leaves with the soil types on which the trees grew and with the amounts of exchangeable REE in the soils. Soils derived from granites and granite gneisses gave hickory leaves with the highest quantities of REE. There was no definite correlation between the RE content of the leaves and that of any other constituent, but there appeared to be some tendency for high RE concentrations to accompany low lime contents, and vice versa. The RE concentrations of mature leaves were 2 to 3 times those of young ones.

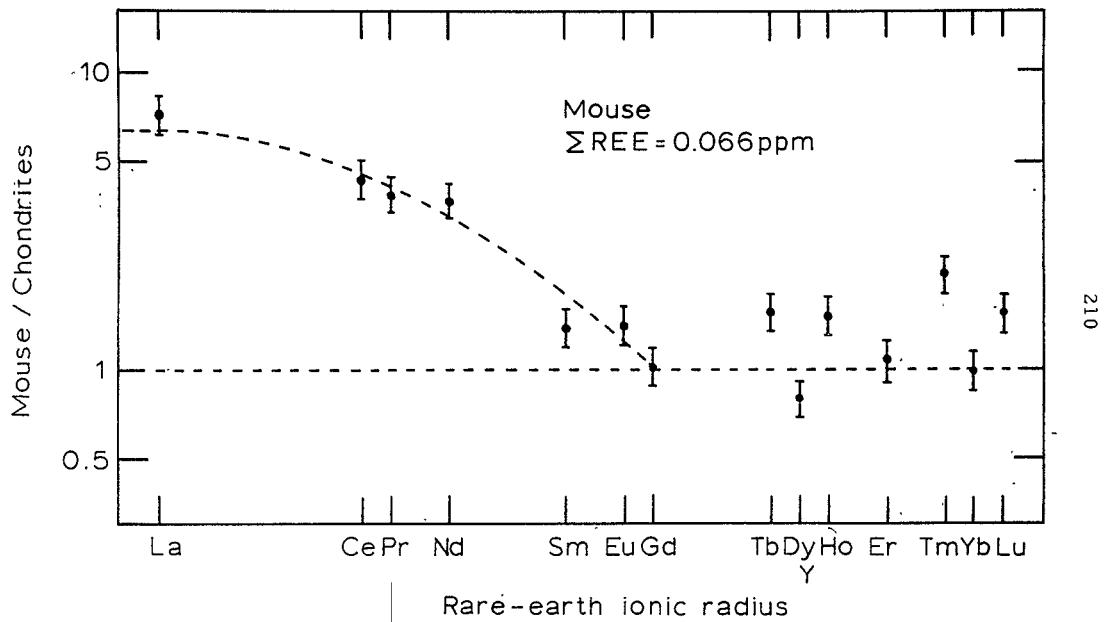


Fig. 51. Comparison plot for a laboratory mouse (Table 40). Upper dashed curve represents the North American composite shale.

Table 41. RE Contents of Some Crop Plants<sup>a</sup>

	<u>REE</u> <u>(ppm)</u>
Alfalfa . . . . .	21-51
Beet (roots) . . . . .	20
Corn (grain) . . . . .	5
Corn (leaves) . . . . .	122
Lima bean (leaves) . . . . .	34
Millet (parts above ground) . . . . .	14
Parsnip (roots) . . . . .	11
Pea (vines) . . . . .	61
Rhubarb (stems and leaves) . . . . .	100
Spinach . . . . .	51
Tomato (fruit) . . . . .	4
Turnip (tops) . . . . .	22

<sup>a</sup>ROBINSON (1943).

It was presumed that the REE were extracted from the soil through the tree roots. When the leaves fell to the ground and decayed, their REE would then have been returned to the soil, remaining in the upper layers where they would be available to other plants with shallow roots.

The soils were tested for extractable REE with solutions of HCl (0.05N), NH<sub>4</sub>Cl, and NH<sub>4</sub>Ac. The quantities of REE which could be extracted decreased in the order in which the reagents are listed. Although NH<sub>4</sub>Ac was the weakest reagent, it removed a higher proportion of REE relative to other extracted materials, ~1 µg to 10 mg from 100 g of soil. The Ce-earth subgroup was found to contribute, on the average, 52 per cent of the total REE in the leaves and 53 per cent of the exchangeable REE from the soils. The soils with the greatest amounts of exchangeable REE produced hickory leaves with the highest RE contents.

The distribution of the REE in a small hickory tree was determined by ROBINSON and EDGINGTON (1945). Small twigs, wood from the trunk, and wood from the taproot all contained about 40-60 ppm REE. Bark from the taproot contained 140 ppm. In another tree from a different location, nut meats contained 5 ppm REE, the shells 7 ppm, the husks 17 ppm, and the leaves 981 ppm.

In a search for biologic fractionation, ROBINSON, BASTRON, and MURATA (1958) determined the individual RE contents of seven groups of hickory leaves and the extractable REE from four soils on which they were grown. The distributions in the leaves were similar, as were the distributions in the soils. The averages of the relative distributions are given in Table 40 and are shown in Fig. 50. The hickory leaves contain a slightly higher proportion of the heavy REE than do the soils. Most noteworthy is the low Ce content of the leaves. Ce is exceeded in concentration by both La and Nd, showing a normal abundance relative to these elements in the extracts of two of the soils, a nearly normal abundance in the third, and a depletion of 4 to 5 times in the fourth. It was postulated that the low Ce content of the leaves was due to oxidation of that element to the +4 state,

which rendered it less readily available for uptake by plants. The two soils with normal relative amounts of exchangeable Ce were collected near the top of the soil profile, where abundant organic matter would be expected to maintain a reducing environment. The soil with an extremely low proportion of available Ce was low in organic matter and perhaps contained mostly Ce<sup>+4</sup>. The relative quantity of extractable Ce was sufficiently raised when H<sub>2</sub>SO<sub>3</sub>, a reducing agent, was used to seemingly well substantiate this hypothesis.

In an ingenious attempt to find a method for determining the origin of smuggled narcotics, PAPPAS, ALSTAD, and LUNDE (1963) determined the RE contents and patterns in opium from several sources. Examples are included in Table 39. The absolute RE contents of opium ash varied from 20 to 150 ppm. Considerable differences in RE pattern were found among the samples. However, none of these patterns represents any reasonable product of chemical or biological fractionation of the distribution expected for soils or rocks.

#### TEKTITES

RE patterns in three tektites, an australite, a bediasite, and a philippinite, were determined by HASKIN and GEHL (1963b). La, Eu, and Dy were determined in an indochinite and a moldavite by CHASE, et al. (1963). The results of these determinations are given in Table 42, and the RE patterns are shown in Fig. 52. The RE patterns of the three tektites for which nearly complete analyses are available are very close to the average for terrestrial sediments. In absolute RE content, the tektites are similar to the North American shale composite.

It is somewhat difficult to establish how similar the RE patterns of the indochinite and the moldavite are to the crustal average. Ratios of La/Eu are included in Table 43. Those for the bediasite, philippinite, and australite are lower than those for the indochinite and moldavite, but all are in line with the distributions found in sedimentary rocks. The differences

Table 42. RE Contents of Tektites (ppm)

	Bediasite <sup>a</sup>	Philippinite <sup>a</sup>	Australite <sup>a</sup>	Indochinite <sup>b</sup>	Moldavite <sup>b</sup>
La	42	33	38	47	5
Ce	----	----	----		
Pr	14.8	10.2	12.6		
Nd	35	31	35		
Sm	4.4	6.9	5.2		
Eu	2.3	1.4	1.5	1.5	0.83
Gd	8.2	5.6	7.7		
Tb	0.61	0.95	0.59		
Dy	----	----	----	5.3	2.8
Ho	1.36	0.94	1.15		
Er	3.6	3.6	4.0		
Tm	0.55	0.57	0.40		
Yb	4.0	3.4	2.6		
Lu	0.47	----	0.36		
Y	31	31	27		
$\Sigma$ REE	230	200	210	----	----
La/Eu	18	24	25	31	35

<sup>a</sup>HASKIN and GEHL (1963b).<sup>b</sup>CHASE, et al. (1963).

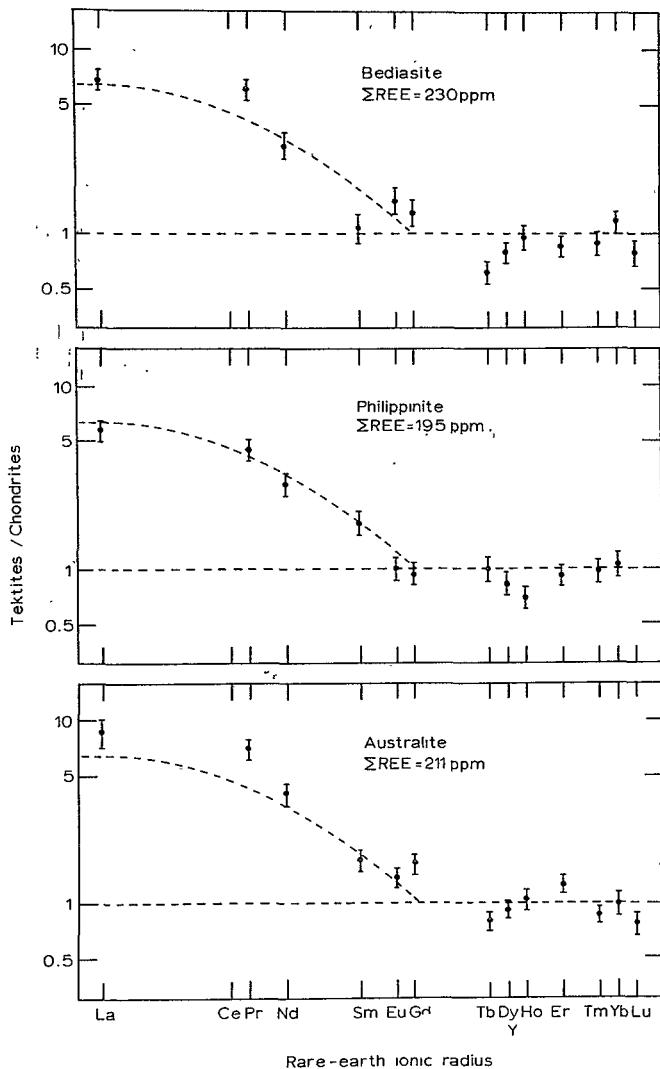


Fig. 52. Comparison plot for tektites (Table 42). Upper dashed curve represents the North American composite shale.

Table 43. Comparison of Ce-normalized RE Distribution of Source Material for Ce-earth Minerals, as Estimated by Masuda, with the Crustal and Meteoritic RE Patterns

	Masuda <sup>a</sup> Estimate	Average for Earth's Crust	Average for Chondritic Meteorites
La	0.55	0.51	0.34
Pr	0.12	0.14	0.14
Nd	0.48	0.49	0.66
Sm	0.12	0.092	0.23
Gd	0.079	0.080	0.37

<sup>a</sup>MASUDA (1957).

are probably due to a systematic experimental error by the two groups of analysts rather than true differences between the tektite groups.

Haskin and Gehl made the following points with regard to the implications of the similarity of the tektite RE patterns and the average terrestrial sediment pattern concerning the origin of tektites. The RE distribution of tektites, as well as the gross element composition and distribution of other trace elements, is most easily accounted for in terms of a terrestrial origin for tektites, as nothing outside the earth is known definitely to have their composition or to be capable of producing it. The strength of any argument for a terrestrial tektite source based on RE pattern depends on the crustal average RE pattern being unique to the earth. If this pattern is dependent for its development upon the particular conditions such as size, temperature, pressure, and time of differentiation, plus perhaps the sedimentary processes for mixing of heterogeneous crustal materials, then it is hard to imagine that it could develop elsewhere in the solar system.

However, it is not known to what extent the crustal average RE pattern is unique to the earth, and a large number of other properties of tektites are quite difficult to reconcile with a terrestrial origin. Thus, it is interesting to consider some of the consequences of extraterrestrial origin for these bodies, including the following: (1) that another body extremely similar to the earth in geochemical differentiation and mixing exists in space; (2) that the tektite parent body was itself once part of the earth; (3) that the crustal average RE pattern is more widely distributed in the solar system than presently seems probable; and (4) that the identity of the crustal average and tektite RE patterns is fortuitous.

#### Eu, Ce, AND Y

The "anomalous" behavior of Eu due to a change in oxidation state has been clearly established in the preceding sections. Most of the observed cases are for igneous processes, but separation in an aqueous environment may have been involved for coals and phosphatic materials. The most

prominent occurrences of anomalous Ce behavior are in the ocean and in soils.  $Ce^{+4}$  may be important in some igneous processes, but this has not been unambiguously observed. The early observations of separation of Sm and Yb through oxidation state change (HABERLANDT, 1947) are not confirmed by recent data.

Which of the heavy lanthanides most closely approximates Y in chemical behavior and what is the effective geochemical ionic radius of Y have been controversial issues for some time. Some assume that Y has a constant behavior relative to the lanthanides, including a constant relative ionic radius. FREY, HASKIN, and POETZ (1965) examined the data for those meteorites whose RE patterns deviated markedly from the chondritic pattern. For each meteorite, the ratios of each of the heavy REE Gd-Y to Y were determined, with the idea that the ratio corresponding most closely to that of chondrites would indicate which lanthanide was nearest to Y in behavior. A similar comparison was made for the average crustal RE pattern and the most fractionated terrestrial RE patterns, those of rock-forming minerals. To minimize systematic errors among different investigators, only meteorites reported by Schmitt and co-workers were used in the meteorite correlation, and only igneous minerals determined by Haskin and co-workers were used in the correlation of terrestrial materials. The strongest correlations were with Ho in the igneous materials and with Tm in the meteorites. The correlations were not sharply peaked in either case, but Y tends to vary in its relative behavior over the entire range of Gd-Yb. A similar variation is found for the behavior of Y in different fractional crystallization and ion-exchange separations. KRUMHOLZ (1964), who has recently reviewed the solution chemistry of the REE, showed that for the REE in complexes with a large variety of organic ligands, the stability constant for Y was not uniquely similar to any given REE but depended on the nature of the complexing ligand. For some ligands, the stability constants of  $Y^{+3}$  were close to those of  $Dy^{+3}$  and for others were more similar to those of  $Pr^{+3}$ . The lack of ligand field

stabilization would tend to move the Y stability constant nearer to that of Gd<sup>+3</sup>. Polarizability effects and/or minor but variable covalent bonding contributions may be responsible for the erratic behavior of Y (SCHWARZENBACH and GUT, 1956). Thus, it is probably not meaningful to try to specify one particular lanthanide as being most closely resembled by Y.

#### THEORETICAL CONSIDERATIONS

The most extensive attempts to formulate a quantitative theory for the fractionation of the REE into their observed patterns have been made by Masuda. In his earliest paper, MASUDA (1957) made use of the data of several analysts on monazite and other light RE minerals. In particular, he was concerned with certain regularities in abundances of the light REE, such as that of Fig. 53. Here, the ratio of Sm/La is plotted versus the Gd/La ratio, and the values are found to lie along a straight line with a non-zero intercept. Similar plots could be constructed for all the light REE, La-Sm, plus Gd. (Data were not available for Eu.) Masuda interpreted these regularities to be the consequence of fractionation of a single, original starting distribution by a mechanism which enriched or depleted the REE as some smooth function of atomic number; i. e., if La is increased relative to Sm in some secondary, derived distribution, then Ce, Pr, and Nd will also be increased in the new distribution relative to Sm, but not by as much as was La, and with Ce relatively increased by more than Pr, and Pr by more than Nd, etc. Insofar as the data can be considered to be represented accurately by a straight line, the extents of fractionation are described quantitatively by the slopes and intercepts of those lines. The regularity shown in Fig. 53, for example, can be written

$$(Sm/La) = m(Gd/La) + b .$$

In a more general fashion, the lines for any of the elements (E) Ce through Sm could be expressed in terms of the end members of the series, La

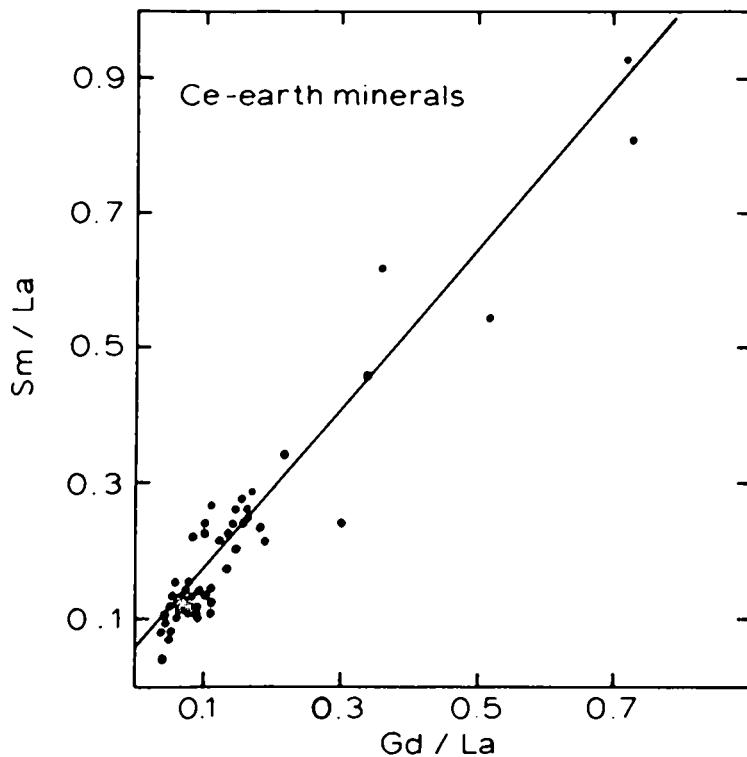


Fig. 53. Plot of (Sm/La) versus (Gd/La) for Ce-earth minerals (after MASUDA, 1957).

and Gd, as follows:

$$(E/La) = m(Gd/La) + b .$$

Thus, the quantity of any element can be written in terms of any two of the others. Generally,

$$E = m Gd + b La .$$

The values of the slopes and intercepts are necessarily related to relative abundances of the REE in their original distribution. MASUDA (1957) was able to estimate this distribution in the following way.

Let it be assumed that the extent of fractionation is a linear function of atomic number. Then the relationship below might be expected to hold:

$$\frac{(E/La) - (E/La)_o}{(E/La)_o} = f \frac{(Gd/La) - (Gd/La)_o}{(Gd/La)_o} ,$$

where  $f$  depends on the difference in  $Z$  of element  $E$  and  $La$ . If the element is  $Ce$ , for example, it will behave more like  $La$  than like  $Gd$  during the fractionation, and  $f$  would be small, as the  $(Ce/La)$  ratio would not change as drastically as the  $(Gd/La)$  ratio. For  $Sm$ ,  $f$  would be large. Masuda gives  $f$  as

$$f = \frac{Z_E - Z_{La}}{Z_{Gd} - Z_{La}} .$$

The above equation can be rearranged to the form

$$E = f (E/Gd)_o Gd + (1 - f)(E/La)_o La$$

This is a linear equation of the same form as the empirical one given above, and if the coefficients are equated,

$$f (E/Gd)_o = \text{slope} ,$$

and

$$(1 - f)(E/La)_o = \text{intercept} .$$

This enables evaluation of the initial distribution of the REE relative to one member of the series. The values obtained are

compared in Table 43 with those for the crustal average and for chondritic meteorites. Clearly, the starting distribution is identical with the crustal average, and the agreement is remarkable. It must be mentioned that no strictly defined, single starting RE pattern is necessary for all the minerals observed, as the regularities are not that accurately described by a line; rather the line is a sort of average describing a trend.

In a later paper, MASUDA (1962) reconsidered his equation and decided that a more nearly accurate form was a logarithmic one, in which the logarithms of the ratios, such as that given below, were used:

$$\log(E/La) = f \log(Gd/La) + b$$

In this equation, the initial relative RE abundances are included in the intercept. Masuda attempted to use this equation for all 14 of the lanthanides and to relate the RE pattern of the earth's crust (based on Minami's shales) with early neutron activation data for chondrites (SCHMITT, et al., 1960). The fractionation of the lightest REE could be well approximated by the equation, but fractionation was also calculated for the heavy REE. Minami's data for the heavy REE were observed not to fit the prediction, and it was suggested that the data were in error. They were somewhat in error, but the better data now available show no apparent fractionation among the heavy REE, so the fit is not improved. In his paper, MASUDA (1962) defined a "separation index" of the form  $(E/La)_{\text{rock}}/(E/La)_{\text{chondrite}}$  and plotted its logarithm against RE atomic number, thus employing the technique used in this paper for display of RE patterns, which was also independently introduced by other investigators (CORYELL, CHASE, and WINCHESTER, 1962; HASKIN and GEHL, 1962).

There are still very few known RE patterns which give a straight line for a plot of the logarithm of the separation index versus atomic number, and most are fairly complicated. MASUDA (1962) showed that some of the more complex patterns could be fitted by successive use of his equation, with appropriate, arbitrary, parameter changes. This

would correspond chemically to a series of fractionations under a variety of unspecified conditions in order to produce the particular pattern under consideration. As many as six separate stages were included. Much of the scatter in the natural patterns is probably due to analytical error, and perhaps the results of curve-fitting with a large number of parameters will provide some insight as to the nature of the separation processes involved.

In the simplest type of separation requiring a linear relationship among the logarithms of the separation coefficients, two types of pattern are produced (MASUDA, 1963a). These are shown in Fig. 54. The straight horizontal line represents the original distribution in a liquid system. The sloped line represents the distribution in the residual liquid following partial crystallization under conditions which are described below, and the curve is the average distribution for the solid formed. The Kilauea-Iki basalt (SCHMITT, et al., 1963) has a "liquid-type" pattern, and the Norton County achondrite (Fig. 3) and the oceanic tholeiitic basalts (Fig. 14) are believed by Masuda to be examples of "solid-type" patterns.

The equilibrium characteristics of systems which would produce such patterns were considered by MASUDA and MATSUI (1963) and MATSUI and MASUDA (1963) in papers beset by mathematical complexity and frequent notation changes which, in fact, led them to some minor circular arguments and perhaps some invalid conclusions. Their model was originally meant to apply to the earth as a system, to produce a solid-type mantle and a liquid-type crust, a situation only roughly justifiable on the basis of the available RE data. It can be applied to a less specific crystallizing system and has the following boundary conditions:

1. Initially, the entire system is molten.
2. The liquid solidifies in a series of small increments. The mass of any increment, say the  $n^{\text{th}}$ , is a constant fraction,  $w_{\Delta_f}$ , times the mass of the residual liquid at the time of solidification of the  $n^{\text{th}}$  increment. The fraction of the total mass of the system which is still liquid at the  $n^{\text{th}}$  stage is designated  $w_l$ .

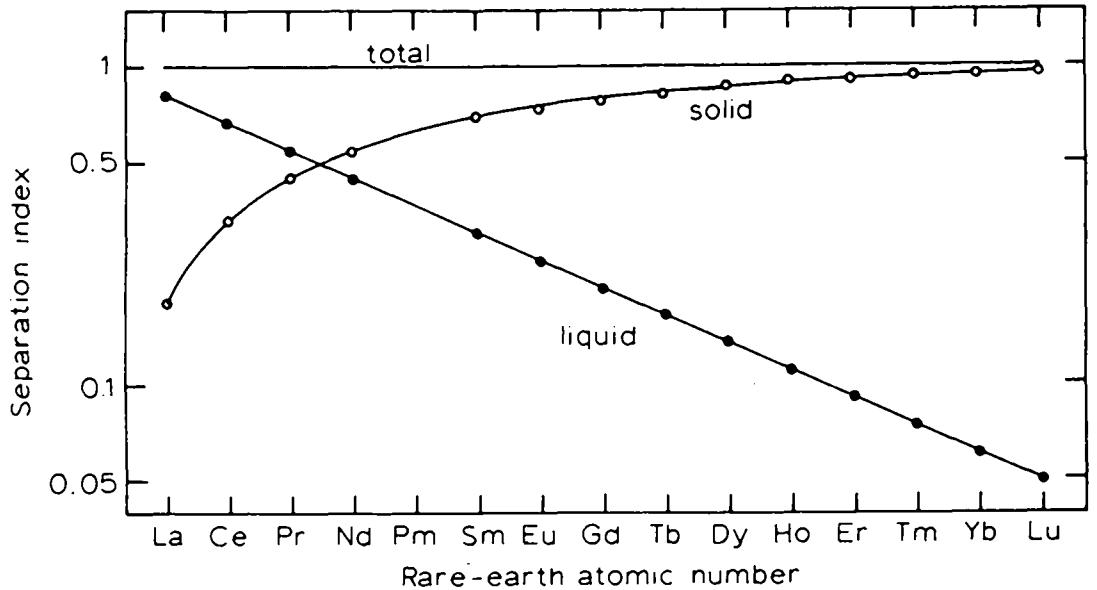


Fig. 54. Comparison plot calculated from theory of MASUDA and MATSUI (1963). Horizontal line represents original liquid system. Sloped line is "liquid-type" plot, similar to that found experimentally for Kilauea-Iki basalt. Curve represents conjugate "solid-type" RE pattern.

3. The mass of a trace element E (not necessarily a REE) which enters the  $n^{\text{th}}$  increment of solid is a constant fraction,  $E_{\Delta_f}$ , of the mass of E still in the liquid at the time the  $n^{\text{th}}$  increment is crystallized.  $w_{\Delta_f}$  and  $E_{\Delta_f}$  are related by a partition coefficient,  $E_k$ , as follows:

$$E_k = \frac{E_{\Delta_f}}{w_{\Delta_f}}.$$

The fraction of the entire mass of E in the whole system which is still in the liquid at the  $n^{\text{th}}$  stage is  $E_{f_n}$ .

4. The partition coefficients for the lanthanide series elements are simply related in the manner which leads to patterns of the type shown in Fig. 54.

5. At some stage, the residual liquid is suddenly quenched to produce a large amount of liquid-type material of uniform RE composition.

The quantities  $E_{f_n}$ ,  $w_{f_n}$ ,  $E_{\Delta_f}$ , and  $w_{\Delta_f}$  were taken to be related as follows:

$$\log w_{f_n} = \frac{-n}{2.303} w_{\Delta_f}$$

and

$$\log E_{f_n} = \frac{-n}{2.303} E_{\Delta_f}.$$

The quantity of interest is the separation index, or the normalized ratio of an element in a rock to the same element in chondrites. This quantity was shown to be equivalent to  $\log (E_{f_n}/w_{f_n})$ , and

$$\log \frac{E_{f_n}}{w_{f_n}} = \frac{n}{2.303} (w_{\Delta_f} - E_{\Delta_f}).$$

This gives only the ratio for a single lanthanide. To obtain the pattern for the lanthanide group, it is necessary to rewrite the equation in terms of the partition coefficient, as defined by the model:

$$\log \frac{E_f}{w_f} = \frac{n w \Delta_f}{2.303} (1 - E_K) .$$

This equation can be rearranged into a form which is exactly equivalent to the following:

$$\ln \frac{I_{N_{Tr}}}{L_{N_{Tr}}} = \ln \frac{I_{N_{Cr}}}{L_{N_{Cr}}} ,$$

in which  $L_{N_{Tr}}$  and  $L_{N_{Cr}}$  are the masses of trace element and crystallizing material, respectively, which remain in the liquid portion of a crystallizing system, and  $I_{N_{Tr}}$  and  $I_{N_{Cr}}$  are the masses of these elements in the entire system. This relationship was first derived by DOERNER and HOSKINS (1925) to describe the crystallization of dilute Ra with salts of Ba. Its application to geochemical systems has been discussed by McINTIRE (1963). It can be simply derived on the assumption that the concentration of a trace element entering the crystalline phase at any instant is proportional to the concentration of that trace element in the mother liquor at that same instant; i.e., only the surface of the crystallizing solid is in equilibrium with the liquid. The proportionality constant is a partition coefficient, identical to the  $E_K$ 's of MASUDA and MATSUI (1963, 1965). It is the addition of a relationship among the  $E_K$ 's for the lanthanides to the equation for such a crystallizing system which makes it possible to predict RE patterns like those shown in Fig. 54. Empirically, a liquid-type RE pattern such as that of Fig. 54 is described by an equation of the form

$$\log \frac{E_f}{w_f} = \text{const. } \Delta Z + \text{const.}' .$$

$\Delta Z$  is the difference in atomic number between lanthanide  $E$  and La. MASUDA (1963a) and MASUDA and MATSUI (1963) point out that this is equivalent to

$$\text{Ce}_{\Delta_f} - \text{La}_{\Delta_f} = \text{Pr}_{\Delta_f} - \text{Ce}_{\Delta_f} = \text{Nd}_{\Delta_f} - \text{Pr}_{\Delta_f} = \dots = d ,$$

where  $d$  is a constant. In other words,

$$E_{\Delta_f} = La_{\Delta_f} + d \Delta Z .$$

It follows that

$$E_k = La_k + \frac{d \Delta Z}{w_{\Delta_f}} ,$$

so if the values of the partition coefficient of  $\text{La}$  and the constant  $d$  are known, the partition coefficients for the rest of the elements in the lanthanide series are known also. Substitution of the expression for  $E_k$  into the earlier form of the equation gives

$$\log \frac{E_f}{w_f} = - \frac{dn \Delta Z}{2.303} + \frac{n w_{\Delta_f}}{2.303} (1 - E_k) ,$$

which has the same form as the empirical equation, with

$$-\frac{nd}{2.303} = \text{slope}$$

and

$$\frac{nw_{\Delta_f}}{2.303} (1 - La_k) = \text{intercept}$$

Unfortunately, Masuda and Matsui attempt to evaluate separately the parameters  $n$ ,  $d$ ,  $w_{\Delta_f}$ , and  $La_k$  by fitting RE patterns, and gain apparent information which is, in reality, ambiguous, because it is not possible to split the slope and intercept unless a completely independent means is available for evaluating part of the parameters. Later in their treatment, they obtain a form of the equation which is equivalent to the Doerner-Hoskins equation, and which does not retain these extra parameters. From it, they obtain partition coefficients for the REE which are legitimate within the framework of their model, with the assumption that the earth's

silicate portion has the same average RE content and pattern as the chondritic meteorites, and that the crust is a residual liquid and the mantle a crystallized solid.

Not satisfied with atomic number as a controlling influence on chemical processes, MASUDA (1963c, 1965a) sought correlations of atomic number with various properties of the REE and found that the reciprocal of RE ionic radius is a close linear function of atomic number, provided that the more recent ionic radii of TEMPLETON and DAUBEN (1954), rather than those of AHRENS (1952) or GOLDSCHMIDT (1926), are used.

Patterns such as those of the Kilauea-Iki basalt and the Kirovograd granite (MASUDA, 1963a; CORYELL, CHASE, and WINCHESTER, 1963) can be nicely fit by the model, but it is inaccurate, well outside of experimental error, to say that the average crustal pattern is fractionated from the chondritic pattern as so smooth a function of atomic number. Thus, the detailed applications of the equations appear to be limited. MASUDA (1963d, 1965b) has had remarkable success, however, in predicting approximate abundances for a large number of elements in terrestrial basalts on the basis of his model for crystallization and partition coefficients proportional to the inverses of the radii of the ions. He has made an interesting attempt to relate the RE patterns of several materials to their depths of origin (MASUDA, 1963b).

#### CRUSTAL ABSOLUTE RE ABUNDANCES; MASS BALANCE ESTIMATES

The order of magnitude of the crustal absolute contents of the REE can be considered to be known with considerable accuracy, because that magnitude is the same for all common rocks. The problem of stating exact values is still a difficult one. The relative abundances of that part of the earth's crust which is involved in the weathering and sedimentation processes can also be considered to be well known, as the average RE pattern for sedimentary rocks is quite precise (Table 28, Figs. 2, 41).

The absolute abundances for the REE in sedimentary rocks must average in the vicinity of 240 to 280 ppm. The average for igneous rocks is less certain, since the major portion of the igneous rocks in the crust is inaccessible to analysis. The usual assumption that the average composition of the crust can be represented by basalt and granite can be invoked. The range in  $\Sigma$ REE for the composite granites is 220 to 320 ppm, and that for the composite basalt is 170 ppm. However, the few individual basalt samples range in RE content from 180 to 630 ppm, while modern analyses on three gabbros and a diabase give considerably lower values of 28 to 123 ppm. If the basalt-like fraction of the earth's crust is like the basalts analyzed so far, the RE content of the crust will be somewhat higher than if it resembles the gabbros and diabase in composition. There are simply not yet enough dependable analyses to know for certain whether the gabbro and basalt RE contents are truly different. Consequently, we recommend the value of  $\Sigma$ REE = 240 ppm for use in abundance calculations and estimates. This is the same RE content as in the composite North American shale, so our present best guess of crustal abundances for the individual REE are those determined analytically for the composite shale, as given in column 3 of Table 28. It does not seem possible, on the basis of present information, that these values for an average crustal RE content could be in error by as much as  $\pm 50$  per cent.

Most previous estimates of the average abundances for igneous rocks have been based on the absolute contents found by Minami for composite shale samples, which correspond to  $\Sigma$ REE = 148 ppm (e.g., RANKAMA and SAHAMA, 1950; MASON, 1958; AHRENS and TAYLOR, 1961; VINOGRADOV, 1956). TUREKIAN and WEDEPOHL (1961) used the relative abundances of Minami, but increased them to  $\Sigma$ REE = 220 ppm, in close agreement with the present estimate.

HORN (1964) has gathered data for all of the chemical elements in as many different rock types as possible. He has divided the crust into various segments and has submitted maximum and minimum literature

values for each element in each segment to a computer programmed to draw up a geochemical balance. A balance was obtained for all elements except those whose crustal concentrations are significantly affected by volcanic emission of volatiles. Horn gives values which sum to 350 ppm for the igneous rock average RE content, which is certainly too high, and to 136 ppm for shales, which is too low. In his model, a high concentration (470 ppm) for REE in ocean sediments results, which is well above the experimentally determined range of 102 to 270 ppm. The use of all reported values to obtain a maximum and a minimum is perhaps too indiscriminate to provide really accurate estimates, and many data not available to Horn were used to obtain our recommended values.

FLEISCHER (1965b) has compiled all the available spectrographic values for the REE and gives values of 37 and 4.6 ppm for Y and Yb in basalts and 52 and 3.7 ppm for Y and Yb in granites. Combining these values would give a somewhat higher average RE abundance for the crust than that based on the composite North American shale, for which the Y and Yb contents are 35 and 3.4 ppm.

The total quantity of REE in the earth's crust can be estimated from the mass of the crust ( $2.4 \times 10^{25}$  g) and its average RE content. This assumes that the weathered part is representative of the whole crust. The averages for La and Yb, for example, are about 39 and 3.4 ppm. On this basis, the crust contains  $9 \times 10^{20}$  g La and  $8 \times 10^{19}$  g Yb. A crust plus mantle (mass =  $4.1 \times 10^{27}$  g) of chondritic composition would contain  $1.2 \times 10^{21}$  g La and  $7 \times 10^{20}$  g Yb. Thus, if the whole earth or the mantle and crust are chondritic, the REE are strongly concentrated in the crust. For the latter case, about 75 per cent of the La and 10 per cent of the Yb are there. Similar enrichment factors are required for many other trace elements. GAST (1965) suggests that such efficient separations cannot be expected to have taken place in a body the size of the earth, and that a cosmochemical concentration may have taken place previous to accretion of the earth with the result that its content of trace elements is much greater

than that of the chondritic meteorites. TAYLOR (1964b) believes that strong concentration in the crust has occurred for all elements which do not readily enter six-fold coordination with oxygen in close-packed structures. He attributes the uniform concentration of the Y-earth elements to the fact that their ions are all smaller than  $\text{Ca}^{+2}$ . For the elements which are larger than  $\text{Ca}^{+2}$ , the extent of concentration in the crust increases rapidly with ionic size.

The geochemical coherence of the REE should make these elements particularly amenable to mass balance calculations. For example, the plausibility of deriving oceanic island alkali basalts from a magma whose residue would be oceanic tholeiitic basalt was demonstrated in an earlier section. Another potential use is the establishment of the relative quantities of basalt and granite which are weathered and mixed to form sediments. The RE abundance pattern and concentrations for shales are fairly well established. Provided that the average granite RE pattern is different from the average basalt pattern, and that these average patterns can be accurately determined and the crust can be adequately represented by granite and basalt, it becomes a simple exercise in algebra to find out what quantities of these two igneous materials must be mixed to give the RE pattern and absolute abundance found in sediments. TAYLOR (1964a) attempted this calculation: with a paucity of data, part of which had to be rationalized away, and concluded that a 1:1 mixture of granite and basalt was needed to provide the sediment pattern. He then proceeded to base a table for the crustal abundances of all the chemical elements on this mixture. It was later reported by TAYLOR (1965) that the absolute RE abundances in his granite and basalt had been omitted in the above calculation and that the inclusion of RE abundances in the calculation drastically changed the ratio to a 1:5 mixture of granite to basalt. Inclusion of abundance data for the REE in basalts from the Atlantic ridge and experimental Mohole resulted in a 1:1 mixture of granite to basalt (TAYLOR, 1965).

Detailed examination of the composite basalt (Fig. 6), which represents the best available estimate of the average for that material, and the composite granites (Fig. 19), indicates that the two cannot be exactly added together (FREY, HASKIN, and POETZ, 1965). The average for the granitic patterns has a heavy element distribution indistinguishable from that for sedimentary rocks, whereas in the basalt pattern, the heavy elements are slightly fractionated. Put more crudely, one would not be much in error to assume that both the granite and basalt patterns are identical to the average sediment pattern except for two elements, La and Eu. La is relatively more abundant in granites and less abundant in basalts than in sediments. The opposite is true for Eu. However, the relative deviations of La and Eu from the sediment pattern are different, so the mixture of granite and basalt which brings the La value in line with the desired sedimentary distribution does not predict the appropriate quantity of Eu. Finally, if it is rationalized that the Eu value is capricious owing to the ability of that element to be separated from the rest of the REE by a mechanism based on an oxidation state change, then a mixture of about six parts basalt to four parts granite yields the sediment curve to within  $\pm 10$  per cent for all the REE except Eu. This is a very reasonable mixture as far as the resulting gross element composition is concerned and is not much different from the value obtained by TAYLOR (1964a).

Unfortunately, the mass balance calculation as described above is not very sensitive to even fairly large changes in the granite/basalt ratio, because of the close similarity between the average granite, basalt, and sediment patterns. As a result, extremely accurate measurements of the average granite and basalt patterns would be needed even to determine whether such a calculation is meaningful..

#### QUALITATIVE SUMMARY OF TERRESTRIAL RE ABUNDANCES

The results of the earliest works on the RE abundances in crustal rocks and minerals, tempered with intuition which was prejudiced by

experience with the difficulties of performing RE separations in the laboratory, led to qualitative concepts of the geochemical behavior of the REE, as reflected in the standard textbooks of geochemistry and by comments in many scientific papers.

The REE have been expected to be a strongly coherent group, whose relative abundances would not be appreciably disturbed by ordinary geochemical processes. The group was considered to move as a single entity that would follow and substitute for  $\text{Ca}^{+2}$  as a consequence of ionic radius similarities. On the basis of the anticipated strong coherence during natural processes, the crustal and primordial RE abundance patterns were presumed to be the same. The bulk of the REE in the crust was known to be associated with the common igneous rocks, but because of the strong tendency of the REE to form their own minerals, they were thought to be present almost entirely in accessory RE minerals, or RE-concentrating minerals. The RE patterns in those minerals were thought to be rigidly selective.

The REE were known to fractionate under sufficiently strong magmatic differentiation. Claims were made that the Ce-earth group consistently became concentrated in the final magmatic stages. The same claim was made for the Yearths. It had been stated that one group collects in the final liquid of granitic magma and the other in magmas of nepheline syenitic composition, but there was no agreement about which group concentrated in which type of residue. Eu and Ce, and perhaps Yb and Sm, were believed to be separated from the rest of the REE as a result of oxidation state changes. The REE, somewhat fractionated in the igneous portions of the crust, were found to be mixed again into their average crustal proportions by weathering and sedimentation processes. RE patterns from separate phases of a differentiated intrusion were expected to resemble each other closely, which would assist in establishing genetic relationships.

While most of these early impressions remain valid today, some are wrong, others incomplete, and others exaggerated because of a change in emphasis with time. For example, the REE are accepted to be a

geochemically coherent group, but the separations within that group are now being stressed as a potential source of information about geologic processes. Some qualitative statements about the geochemical behavior of the REE, based on the more extensive and accurate data now available, are given below. Few of them are original to this paper, most having been set forth in the papers in which the data were presented. In addition, several interpretive papers have appeared (e. g., TAYLOR, 1960, 1962; AHRENS, 1964a; FLEISHCHER, 1965b; JENSEN and BRUNFIELD, 1965), and (a particularly useful one) BALASHOV (1963a).

The existence of a RE pattern characteristic of the earth's crust has been firmly established by the analyses of many sedimentary rocks, among which relatively little pattern variation is observed. This crustal pattern is genetically related to the presumed primordial pattern that is found in chondritic meteorites. However, in the crust, the light REE relative to the heavier REE are increasingly enriched in the order Sm-La as compared with the corresponding chondrites. This is presumed to be a result of the zoning of the earth into core, mantle, and crust. The crustal absolute RE content is much higher, by a factor of  $\sim 50$ , than that of chondrites, but not enough so to preclude a whole earth, or crust plus mantle, of chondritic composition. The relative, if not the absolute, RE pattern of the whole earth is very probably like that of chondrites.

The bulk of the REE in the crust is dispersed among the common igneous rocks and sediments. Although a significant portion of the REE is found in accessory RE minerals and RE-concentrating minerals, the major fraction is contained in, or intimately associated with, the main, rock-forming minerals. The REE do constitute a geochemically coherent group and are therefore particularly valuable to the determination of abundance relationships, but the group is far less coherent than previously thought. No examples of magmatic differentiation have been carefully examined in which the members of this group did not fractionate. Fractionation often results in partial separations among all or many of the REE,

and analysis for most of the REE is required in order to show . . . fractionation.

The RE patterns and contents in the various minerals of a single rock can be very different. Thus, partition of the REE among rock-forming minerals is one plausible mechanism for production of different whole rock patterns. Partition of the REE between liquid and solid phases is another. Mafic minerals appear to have higher absolute RE contents than light minerals, except for Eu, which concentrates strongly in feldspars as a result of its reduction to the +2 oxidation state. The relative RE distributions of feldspars contain a higher proportion of the light REE than do mafic minerals from the same rock. Many of the minerals in which the REE are essential components or are quantitatively significant are markedly selective in their RE patterns. This selectivity is less rigid than formerly supposed. The variability of RE patterns for a given mineral is dependent on both crystallochemical and geologic factors.

On the average, there are increases in both total RE content and the relative proportion of the light REE in the order ultrabasic, basic, acid rocks, but this is strictly an average phenomenon, as patterns and contents vary among the individuals of any type, leading to considerable overlap.

Members of either the Ce- or Y-earth subgroups can predominate.. in the final stage of a differentiation sequence. There is no simple correlation between RE pattern and content and the acidity, basicity, or content of any major element in a magma. This also holds for Ca, although that element is still believed to control RE behavior to a considerable degree. There is some evidence indicating that the light REE may tend to concentrate in the final liquids from magmatic crystallization, unless liquids with high alkali and fluoride or carbonate contents are involved, as these preferentially retain the heavy REE as complexes. Such liquids are important in metasomatic processes.

The average RE patterns and contents of granites and basalts are consistent with the derivation of sediments from materials which can be represented by about equal quantities of those two rock types.

Weathering processes acting on igneous rocks mix their REE well enough to give patterns which are close to the crustal average. Patterns vary relatively little among different sediment types. Under appropriate conditions, however, sedimentary processes do fractionate the REE significantly in a manner which can be correlated with sediment type and with distance from the source. Aqueous transport of the REE both in particulate and colloidal forms and as dissolved ionic and complexed species is geochemically important. The RE contents of both ocean and ground waters are extremely low, and the RE patterns have higher proportions of the heavy REE than the crustal average. Concentration of the REE into phosphatic sedimentary materials is common.

Relative to their Ca contents, the RE concentrations in animal tissue, including bone, are very low. On the average, the RE contents of plant material are higher than that of animal tissue, and in the case of hickory leaves are very high on an absolute basis. No strong fractionation of the RE group by biologic organisms is apparent, but a limited selectivity in favor of the heavy REE is indicated.

Studies of RE fractionation as an indicator of geologic processes appear promising, but have barely begun to be exploited.

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